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SUPERINTENDENCE AND

CHEMICAL INVESTIGATION OF INDIAN LICHENS

Part XXI. Occurrence of Fallacinal in *Teloschistes flavicans*

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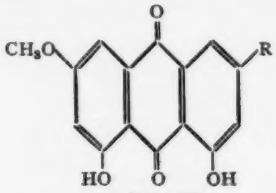
Received September 18, 1958

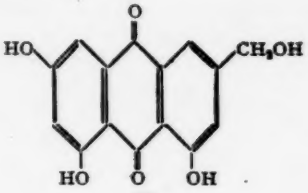
In an earlier study[1] of the Indian sample of *Teloschistes flavicans*, besides physcion (I) and a colourless substance, the existence of teloschistin was recorded and its constitution elucidated as ω-hydroxyphyscion (II).[1-2] Subsequently, its synthesis[3] was also effected by the action of N-bromosuccinimide on physcion diacetate followed by the action of silver acetate and final hydrolysis. The melting point of teloschistin, obtained from the lichen, was first recorded as 228–30° but the synthetic sample was found to melt higher (245–47°). However, purification of the natural sample by the preparation of its acetate and subsequent hydrolysis raised the melting point to 244–46° alone or mixed with the synthetic sample. The acetates of the synthetic and natural samples agreed closely and the mixed melting point was undepressed.

More recently, Murakami[4] examined the pigments of *Xanthoria fallax* and found that this lichen contains besides physcion (I) and teloschistin (II) the corresponding aldehyde, fallacinal (III). He also recorded the melting point of teloschistin as 235°. Consequently, we have repeated the study of *T. flavicans*; but the new collection made in 1955 appears to be somewhat different particularly in its colour. Adopting the procedure described in the earlier publications we have now obtained a product which even without purification through its acetate melted much higher (246°) and after purification by the acetate method, the melting point went up to 250–52°. Further, in all its properties it agreed with the description of the aldehyde, fallacinal (III). In order to have an effective separation of the components and have a quantitative idea of the composition, the aldehyde was removed as the 2:4-dinitrophenylhydrazone or by means of Girard's Reagent-T and the remaining portion examined. It was found to be almost pure physcion. In one experiment the mixture of components was subjected to oxidation with active manganese dioxide in order to oxidise any teloschistin that may be present. But it was noticed that this did not make an appreciable difference in the yield of fallacinal. The results of the present series of experiments lead

to the conclusion that the sample of the lichen now examined contains physcion (I) (80%) and fallacinal (III) (20%) only as the coloured components and that teloschistin (II) is almost absent. It differs from the earlier sample which contained besides physcion (I), teloschistin (II).



I R=CH_3
II R=CH_2OH
III R=CHO



IV

In order to make sure of the melting point of teloschistin, we have now prepared it by the partial methylation of synthetic citreorosein[5] (ω-hydroxy-emodin) (IV). Earlier Anslow *et al.*[6] employed sodium methoxide and methyl iodide for this purpose and recorded a melting point of 229–31°. As a more convenient method, we have now employed a little less than one mole of dimethyl sulphate and excess of potassium carbonate. The product consisted of the monomethyl ether along with a small amount of the unchanged compound, which could be easily removed by extraction with sodium carbonate. Teloschistin (II) obtained by this method is easily purified and the pure compound is found to melt at 243–44°; this melting point has been checked a number of times and seems to be the most acceptable.

EXPERIMENTAL

The present sample of the lichen, *T. flavicans*, was collected in summer 1955 and it was found to be less coloured than the sample used earlier[1] (collected in 1947).

The air-dried lichen (500 g.), in coarse powder form, was extracted with hot chloroform (3×1 L) and filtered. The total extract was concentrated to about 200 c.c. and an equal volume of ethanol added. On allowing to stand overnight a red crystalline solid separated which was filtered (1·3 g., fraction A). The filtrate when worked up gave the colourless substance[1] along with a small quantity of physcion.

Separation of fraction A

(i) *By crystallisation.*—When crystallised from benzene or a mixture of chloroform and ethanol orange-red needles, m.p. 245–46°, were obtained. This solid was insoluble in aqueous sodium bicarbonate and sodium carbonate,

but soluble in aqueous sodium hydroxide giving a purple-red solution from which a violet precipitate separated on standing. It gave a reddish brown colour with alcoholic ferric chloride and an orange-red solution with concentrated sulphuric acid. With 2: 4-dinitrophenylhydrazine, it formed the hydrazone, m.p. 320–22°. It closely agreed in its properties with fallacinal.[4] The lower melting point was due to contamination with a trace of physcion, the presence of which was shown by vertical paper chromatography. The sample was therefore acetylated using acetic anhydride and concentrated sulphuric acid. The acetate was purified by crystallisation from ethyl acetate when it melted at 181–83° (Murakami[4] reported a melting point of 179–81° for fallacinal tetra acetate). On deacetylation with methanolic sulphuric acid it yielded pure fallacinal, m.p. 250–52°. The infra-red spectrum of this sample was found to agree with that of fallacinal isolated by Murakami.[4]

The chloroform-ethanol mother liquor from the crystallisation of the aldehyde was concentrated to a small bulk, when physcion was obtained as orange-red needles and plates. It was purified by crystallisation from a mixture of chloroform and ethanol, m.p. 204–06°. Yield, 1·0 g.

(ii) *By using* 2: 4-*dinitrophenylhydrazine*.—The mixture (0·25 g.) was dissolved in ethanol and chloroform (1: 2, 180 c.c.) at room temperature and to the orange-red solution an ethanolic solution of 2: 4-dinitrophenylhydrazine (0·17 g.) was added. The mixture was refluxed for 15 min. and allowed to stand at room temperature for several hours to complete the separation of the hydrazone. It was filtered, washed with sulphuric acid (5 N) and then with water, m.p. 320–22° agreeing with fallacinal dinitrophenylhydrazone.[4] Yield, 0·085 g.

The filtrate was concentrated to ⅓ vol. by distilling off the organic solvents under reduced pressure when orange-red needles were obtained. This solid was filtered, washed with sulphuric acid (5 N) and then with water. It crystallised from chloroform-ethanol mixture, m.p. 204–06° (0·18 g.). It agreed with physcion in every respect. In order to test for the possible presence of teloschistin, it (0·17 g.) was dissolved in benzene (30 c.c.) and active manganese dioxide (0·35 g.) was added and the mixture refluxed for 16 hours. The hot solution was filtered from manganese dioxide which was washed several times with hot benzene. The filtrate and the washings were collected and benzene was evaporated off completely. The residue was found to melt at 204–06° and did not give any hydrazone with 2: 4-dinitrophenylhydrazine and further crystallisation did not raise the melting point.

In another experiment the separation of fraction A was effected after treatment of the mixture (fraction A) with active manganese dioxide as given

above. The quantities of the hydrazone and physcion obtained were found to be approximately the same.

(iii) *By using Girard's Reagent-T.*—The mixture (0·5 g.) was dissolved in dioxan (20 c.c.) containing glacial acetic acid (2 c.c.) and a solution of Girard's Reagent-T (0·28 g. in 1 c.c. of water) was added. The mixture was refluxed for an hour, water added to the cooled solution and left overnight in the refrigerator. The precipitated orange-yellow solid was filtered, washed well with water and dried (0·35 g.). It was free from the aldehyde and did not give the dinitrophenylhydrazone. It had however an indefinite m.p. and hence it was methylated in dry acetone medium using excess of dimethyl sulphate (3 c.c.) and anhydrous potassium carbonate (6 g.) by refluxing for 30 hours. The crude dry methyl ether was dissolved in chloroform and chromatographed on alumina, when two bands were obtained. The lower band which was yellow in colour was eluted with chloroform. On evaporating off the solvent, a crystalline yellow solid was obtained which on crystallisation from a mixture of chloroform and ethyl acetate yielded bright yellow-needles, m.p. 224–25° (0·30 g.) undepressed by admixture with physcion dimethyl ether.

The light-red upper band could not be eluted with any solvent. Hence it was taken out and extracted with hot chloroform after treatment with hydrochloric acid. The residue obtained after evaporating the pale yellow chloroform extract was too small for characterisation, but was found to give a brown colour with alcoholic ferric chloride. The red band may therefore be due to a very small quantity of incompletely methylated product from physcion.

Partial methylation of citreorosein (ω-hydroxyemodin) (IV)

To a solution of citreorosein[5] (m.p. 288°, 0·17 g.) in dry acetone (25 c.c.), potassium carbonate (0·5 g.) and dimethyl sulphate (0·05 c.c.) were added and the mixture refluxed for 4 hours on a water-bath. The original intensely purple-red solution gradually changed to reddish brown and some red crystalline solid separated. Acetone was filtered and the residue was treated with water when an orange-yellow solid was obtained. Some more of it was obtained when acetone was evaporated from the above filtrate and the residue treated with water. The combined solid was ground with aqueous sodium carbonate (5%) several times till a fresh extract with the carbonate was not coloured. It was washed well with water and crystallised twice from ethanol when teloschistin was obtained as orange-yellow needles, m.p. 238–40° (0·110 g.). The carbonate extract on acidification yielded a small quantity of citreorosein (25 mg.).

The above sample of teloschistin (0·1 g.) was acetylated with acetic anhydride (1 c.c.) containing a drop of concentrated sulphuric acid and the acetate crystallised from ethyl acetate, when teloschistin acetate was obtained as yellow needles, m.p. 193–94° (0·11 g.), mixed m.p. with teloschistin acetate prepared from physcion through the NBS reaction[3] was undepressed. The acetate was deacetylated using methanolic sulphuric acid. Teloschistin crystallised as orange needles from benzene, m.p. 243–44° (0·06 g.) undepressed by admixture with the sample obtained by the NBS reaction.[3]

Oxidation of teloschistin

Synthetic teloschistin (0·02 g.) was oxidised with active manganese dioxide in benzene solution as carried out in an earlier case; the oxidation product crystallised from benzene as orange-yellow needles (12 mg.), m.p. 250–51° alone or when mixed with fallacinal isolated from *T. flavicans.*

Summary

A sample of *Teloschistes flavicans* collected in summer 1955 was found to contain physcion and fallacinal in the proportion of 4:1 and did not contain any appreciable amount of teloschistin. A pure sample of teloschistin has been obtained by the partial methylation of citreorosein using methyl sulphate and potassium carbonate and is found to melt at 243–44°. On oxidation with manganese dioxide it has yielded fallacinal.

Acknowledgement

We thank the Council of Scientific and Industrial Research for financial assistance and Messrs. Sadtler & Co. for infra-red spectrum.

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ELECTROCHEMICAL BEHAVIOUR OF ZINC IN ALKALINE SOLUTIONS

Part II. Constant Over-Voltage Measurements

BY INDRA SANGHI* AND M. FLEISCHMANN

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(Communicated by Dr. K. S. G. Doss, F.A.SC.)

ABSTRACT

As the whole passivation phenomenon in the case of zinc is very quick and sudden and as it cannot be fully studied and followed by galvanostatic techniques alone, the constant over-potential technique has, for the first time, been applied to zinc and results reported. A special apparatus consisting of suitable oscillator, modulator, demodulator and a stable D.C. amplifier with a gain of 100,000 was used for the purposes and is described. Potential curves for equilibrium current rates, achieved in 0·1 V. and 25 mV. steps after 1 minute each, have been obtained in 6 N, N, 0·1 N KOH and zincate solutions for the complete range of $-1{\cdot}3$ to about $-2{\cdot}0$ volts with reference to Hg/HgO/KOH reference electrode. It has been found that in the first truly active region, the main electrode reaction is the formation of zinc ions while after the passivation it changes to gas evolution. Potentiostatic techniques reveal intermediary stages, undisclosed by constant current methods, of pseudo-passivation and current-plateau regions in which the anodic layer thickens, controlled by the high field cation transport. These observations and explanations are further supported by plotting rate-time transients obtained by suddenly dropping the potentials from higher to lower values, when the rates were found to cut off. Some anomalies and sudden reversal of currents with increasing over-voltages, have also been fully discussed. The influence of other factors, *e.g.*, concentration, stirring, sudden changes in over-voltages, presence of zincate, sulphate, etc., has also been considered. Studies such as these are found to throw considerable light on the electrochemical behaviour of zinc.

INTRODUCTION

FROM a study of the electrochemical behaviour of zinc using constant current methods, which has already been reported[1] it became evident that for a fuller

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understanding of electrode processes and especially for the elucidation of electro-kinetic rates and their variations both steady and non-steady state analyses are necessary. This is even more important in the particular case of zinc, as there is a sudden passivation jump in potential as large as 3–4 volts, because of which the intermediate over-voltage ranges remain inaccessible at any current density used. Constant over-voltage measurements, on the other hand, provide an excellent means to examine all the reactions, slow or fast, stable or unstable, to their completion, over a wide range of rates. Since the rate-constants controlling electrochemical reactions are chiefly potential dependent, they can be kept constant, during study by this procedure. Current-time curves can then be analysed fully as shown by Fleischmann *et al.*[2] A preliminary study by this method has, therefore, been made in order to obtain an insight into what happens between the active and passive states of zinc, especially as such measurements have not primarily been reported in literature, so far.

Experimental

Polarising and Measuring Circuit.—A block diagram of the circuit used to apply and control constant over-voltages is shown in Fig. 1. As already reported,[2] the electronic components were built by Dr. Fleischmann in these laboratories and essentially consisted of:—

High Gain Regulator.—Due to the difficulty of getting a stable D.C. amplification at hundred-thousand times a modulated carrier wave amplifier,

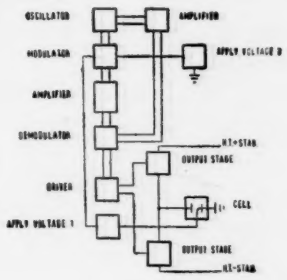

Fig. 1

using a phase sensitive demodulation, was employed. It had a bridged output stage with two valve systems one above and one below the earth potential and consequently regulated both + ve and − ve currents.

Push-pull descrimination was greater than 10,000: 1 and consequently voltages could be accurately superimposed. An additional oscilloscope

monitor was used to ensure that the feed-back loop was unconditionally stable under all working conditions and ranges, and current-time transients were accurately measured either by a multi-microammeter or by an oscilloscope.

Cell and Solutions.—A small convenient cell, with anode and cathode compartments separated by a fine sintered glass disc, was used. Arrangements were also made to stir the solutions by bubbling hydrogen through the cell, when required.

Reference Electrode.—The Hg/HgO/KOH system was used as reference electrode, the actual construction of which was such as to avoid any external bridge while at the same time incorporating a " Luggin " capillary as described in the previous paper.[1] An effort was made to avoid all liquid-junction potentials by using the same concentration of KOH in the reference electrode as in the experimental cell but it was found that in the case of Hg/HgO/KOH (0·01–0·1 N), oscillations were set up even though the push-pull cathode-follower coupled to the modulator, took only 2×10^{-9} A as input current. The reason for this is not quite clear but on measuring the resistances, under the actual cell conditions, it was found that it was about 3 K ohms for normal, 16 K ohms for decinormal and more than 100 K ohms for centinormal reference electrodes. The normal reference electrode was therefore used with all the solutions.

Blank Test.—An estimate was made to find out the change in the concentration of 0·01 N KOH solution in the cell due to the use of a normal reference electrode during the course of an average experiment. It was found that the concentration of the cell-solution did not increase by more than 1%, which was considered negligible for our measurements.

Technique.—Preliminary measurements in normal solution showed the form of the I–V curves, which indicated the necessity of increasing the voltage stepwise since large currents temporarily flowed at each increase. Steps of 0·1 V. were, therefore, arbitrarily chosen for most of the experiments and were taken after one minute each, the current being measured after 45 secs. The same procedure was adopted and I–V curves were obtained for KOH solutions both with and without ZnO or stirring. On reaching various potentials, after 5 mins. the voltage was dropped to other fixed values and the current-time transients taken.

All solutions except 6 N KOH were boiled just before use for 5 mins. and then cooled in closed bottle to remove dissolved oxygen, which may lead to complications.

After some preliminary experiments it was thought that some scatter in results could be caused by variation between different zinc electrodes, even though taken from the same sheet. Later, therefore, various groups of experiments were carried out using one and the same electrode, which was polished and coated off, as previously described, between successive experiments.

It was decided to make a much more detailed study of the behaviour of zinc in 0·01 N KOH solution due to the following reasons:—

(*a*) It is possible to use any voltage steps in 0·01 N KOH since the rate of reaction becomes limited by the diffusion of OH^- ions.

(*b*) Since oxides are not so soluble in this concentration the electrode layers tend to behave as barrier layers thereby permitting measurements of the rate of growth, without the attendant complications of significant chemical dissolution. It is believed that in more concentrated solutions the measured current rates are primarily dependent, not on layer growth, but on precipitation and dissolution phenomena. Evidently, this point seems to have been overlooked by previous workers.

(*c*) In such dilute solutions the active state of zinc is almost absent and therefore the initial part of the anodic behaviour is somewhat simplified, *e.g.*, no black layers are formed but under all conditions only thin transparent layers are obtained.

(*d*) The maximum current changes involved in any study in such dilute solutions are well within the working capacity of the apparatus.

So, in the cases of 0·01 N KOH solutions some other additional procedures were also used to measure and clarify various aspects.

Results

For convenience and quick comparison, all results are shown graphically in Figs. 2 to 10. The potential-current curves in 6 N, N/10, N and N/100 solutions, both under the conditions of stirring and non-stirring and the presence and absence of zincate ions, are shown in Figs. 2, 3, 4 and 5 respectively. As already mentioned, these curves were obtained by increasing the voltage in steps of 0·1 V. and 1 min. and noting the current after 45 secs. of each increase. But, certain additional data, in which the potential is raised in 25 mV. steps, were used, as justified and explained later, to get a more accurate plot of the curves in the voltage range $-1{\cdot}5$ to $-0{\cdot}6$ V. (*Vide* Fig. 8).

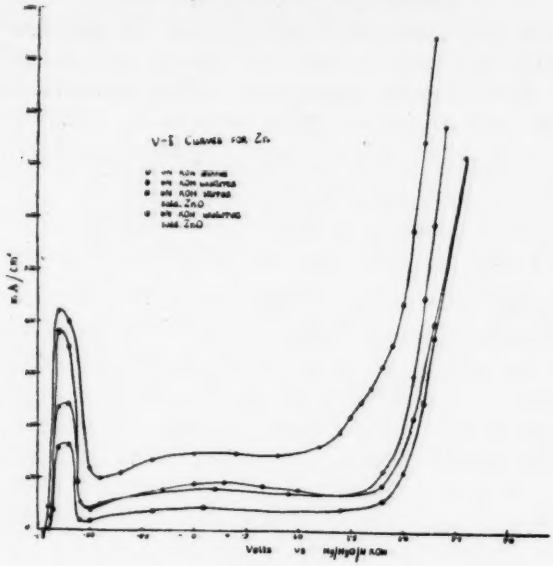
V-I Curves for Zn
mA/cm²
Volts vs Hg/HgO/M KOH

FIG. 2

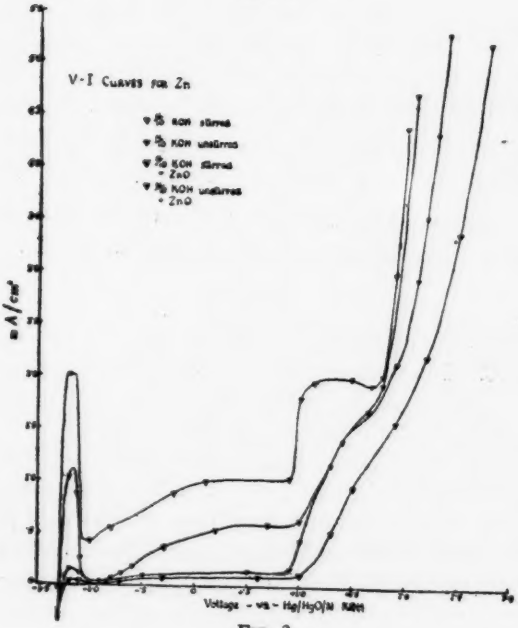
V-I Curves for Zn
mA/cm²
Voltage - vs - Hg/HgO/M KOH

FIG. 3

Additional results were obtained in N/100 solutions by raising the potential of the electrodes, in steps of 0·1 V. after every minute, to 1·8, 1·0, 0·5 and 0·0 V. respectively, leaving them at those potentials for 5 mins. and then suddenly dropping the voltages to various values. The equilibrium

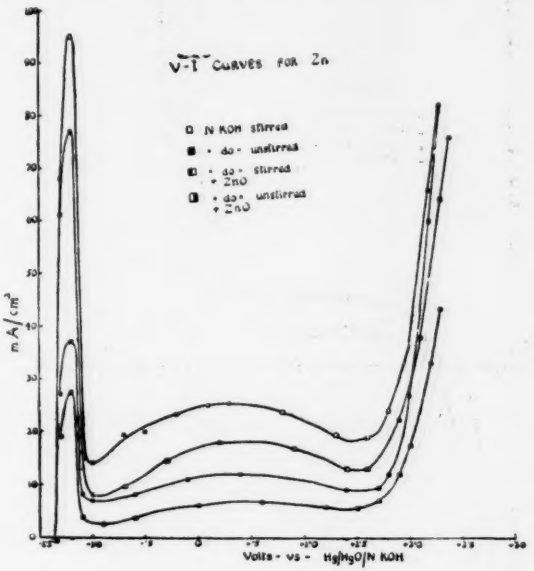

FIG. 4

rates were also obtained by raising the potential in one step from — 1·3 V. to various values and then noting the currents after 30 mins. These data are shown in Fig. 6.

Since it is not possible to show all these V–I curves in one figure on a linear scale, a comprehensive plot on a logarithmic scale is given in Fig. 7 for all the above solutions, concentrations and conditions. Fig. 8 shows a similar logarithmic plot for stirred solutions only, in which the potentials were raised in steps of 25 mV. after 1 min. at each stage, the currents being measured after 45 secs.

Figs. 9 and 10 show rate-time curves in 0·1 N and N solutions, obtained on dropping the voltage from 1·8 to 0 volts. All the potentials mentioned here are as usual, with reference to the Hg/HgO/KOH electrode. The points shown on the graphs are only a fraction of the total points obtained and serve merely to identify the various lines.

Effect of Stirring.—The differences in the current rates in stirred and unstirred solutions are seen to go through a maximum with increasing con-

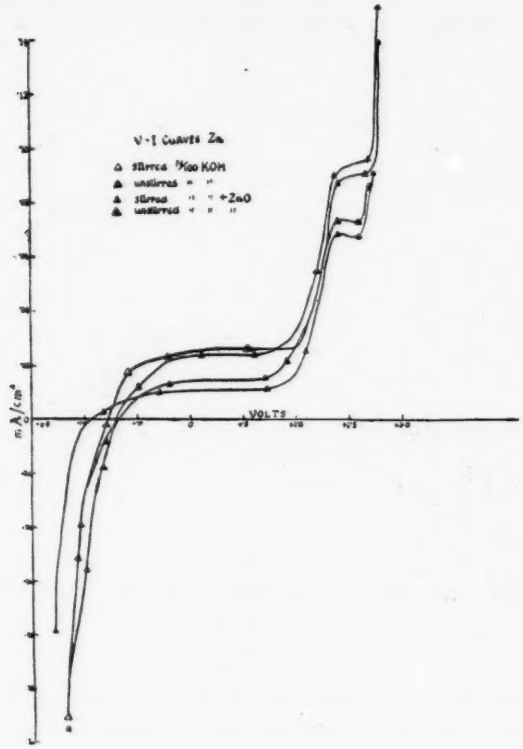

FIG. 5

centration if the curves in Figs. 2, 3, 4 and 5 are studied and compared. This can be visualised in terms of the following argument:

(i) Rate of attack of the electrode increases more rapidly than the limiting current rate as the concentration is increased. This leads to a factor which tends to increase the differences between stirred and unstirred solutions as the concentration increases.

(ii) However, convection due to density differences also increases with the rate of attack and this tends to decrease the differences in stirred and unstirred solutions with increasing concentrations.

The net result of the simultaneous variations in the above two effects can be expected to lead to a maximum in the differences between stirred and unstirred solutions. In order to avoid these complications, it is essential to compare the results only in stirred solutions and this is also emphasised by the curves shown in the abovementioned figures.

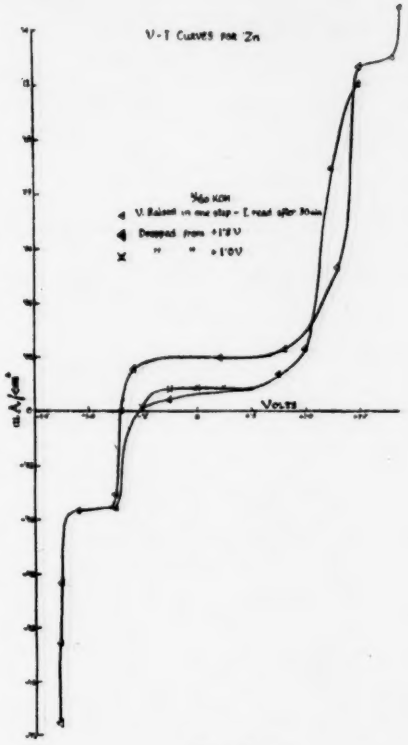

FIG. 6

DISCUSSION

Concentrated Solutions.—Comparison of Figs. 7 and 8 shows that in 6 N and N solutions under all conditions and in N/10 KOH solution under certain conditions, the current rates at each voltage are virtually independent of the time taken to reach that particular potential. Furthermore, the current rates taken after 45 secs. when the voltage is raised in 0·1 V. steps, are very close to the equilibrium rates finally obtained when the potentials are dropped to those values from higher potentials shown in Figs. 9 and 10.

This justifies the use of data taken at 25 mV. steps to construct the details of the initial active portions of the graphs in Figs. 2, 3 and 4, and provides a basis for further theoretical discussion of the V–I curves, apparently determined under arbitrary procedures.

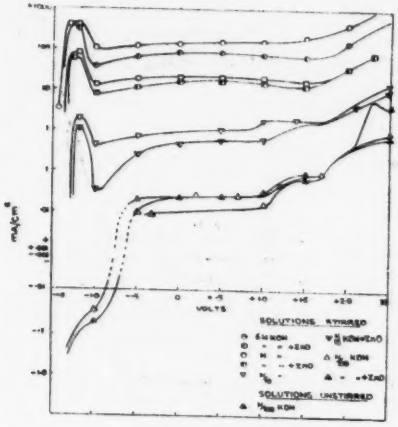

FIG. 7

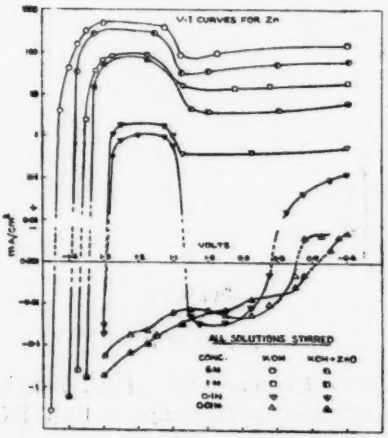

FIG. 8

Active Dissolution.—In all solutions of concentration above N/10, the electrode first shows an initial active region in which the current increases rapidly with voltage as it is made more +ve from about −1·3 V. In this

region zinc actively goes into solution as zincate ions. The data show that there are only small differences between KOH and KOH saturated with ZnO in 6 N and N solutions. Consequently, saturated zincate solutions can still actively dissolve zinc, ZnO and $Zn(OH)_2$ being presumably precipitated in the bulk of the solution, later on. This is in agreement with our

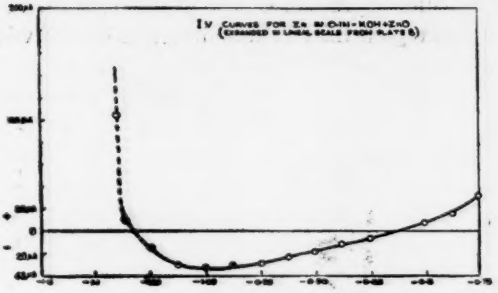

FIG. 8 A

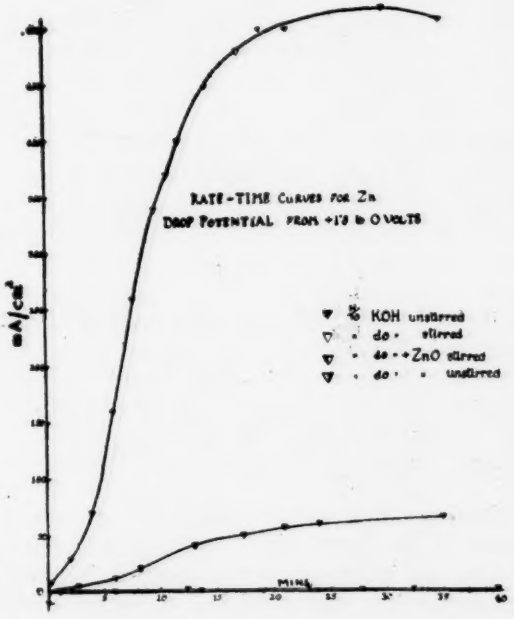

FIG. 9

previous results and those of Dirkse.[3] As far as the electrode surface is concerned, not much precipitation appears to take place in the ascending portion

of the V–I curves. It seems, therefore, that the zincate ions are relatively stable under supersaturation conditions.

The rate of anodic dissolution, however, does not continue to increase with increasing voltage, but soon reaches a maximum value. Although this maximum rate increases markedly with increasing concentration yet it is only a fraction of the limiting rate of OH^- ions diffusion even in 6 N solutions. In this maximum rate region the electrode becomes coated with a visible grey

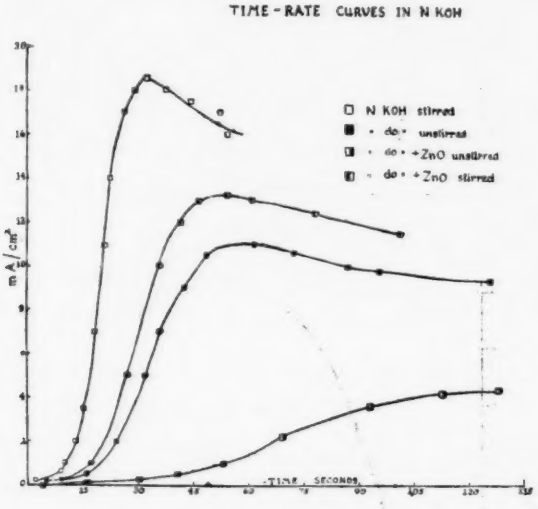

FIG. 10

deposit. In N/10 KOH saturated with ZnO, marked oscillations of amplitude 0·5 mA. and periodicity 0·6 cycles/sec., are set up in this voltage region. On increasing the voltage in successive steps in this current-plateau region, current-time transients are obtained, the rate being initially high and then dropping to the equilibrium value. It may, therefore, be presumed that they are due to a film thickening process.

Pseudo-passivation.—At a certain voltage the rate suddenly starts to decrease, the length of the current plateau being dependent on the concentration of the solution and being completely absent in N/100 solution. In all solutions in the descending portion of V–I curves marked oscillations, as previously mentioned for N/10 solutions, are obtained. These oscillations can only be explained by assuming that either the electrode has two surface layer states in which it can actively go into solution, the formation of either

state retarding the rate of formation of the other, or the $(OH)^-$ ion concentration is repeatedly depleted and replenished at the electrode surface. It is possible that one of the states is zinc and the other a soluble zinc oxide, the maximum rate in the current-plateau region, depending not on the OH^- diffusion, but on the maximum rate of dissolution of the soluble oxide present on the surface. The factors affecting this rate of dissolution are however not yet quite clear. An apparent examination of V–I curves in Figs. 2, 3, 4 and 5 suggests that the rate of dissolution increases markedly with OH^- ion concentration and would appear to be connected with this in some manner. But since the solubility of ZnO in KOH increases with concentration,[4] the zincate equilibrium having some form of equation such as $ZnO + H_2O + 2\,OH^{--} \dashrightarrow Zn(OH)_4^{--}$ it would be expected that the percentage differences in maximum rates between KOH solutions and KOH solutions saturated with ZnO would increase with increasing concentration. For example, if it is assumed that the effect of zincate ions is merely to reduce the free (OH^-) which is the main controlling factor then the differences in zincate and non-zincate solutions should be negligible in N/100 and N/10 solutions and greatest in 6 N solutions. However, experimentally the greatest differences are found in N/10 solutions while in N/100 there are none and in 6 N they are much less than expected. This shows that although (OH^-) tends to increase the rates, yet the zincate ions exert a marked but variable influenec of their own and thereby complicate the behaviour. For example, in N/10 solutions the zincate ions retard some part of the dissolution process. So, it seems that there are at least two reactions in different parts of the curves. One of these can be accelerated and the other retarded by zincate ions under certain conditions. This behaviour of zincate ions appear to be connected with the varying degree of its preferential adsorption in different potential regions and concentrations.

On increasing the voltage from about $-1{\cdot}1$ to $-1{\cdot}0$ V. and taking the transients, the current is first seen to drop to very low values and then rapidly increases with time to the equilibrium values shown. The electrode potential at this stage may be taken to have increased sufficiently to enable the precipitation and formation of a new oxide phase, which seems to be relatively less soluble, thereby decreasing the rate suddenly. This insoluble oxide may however be converted gradually to the soluble form at the oxide/solution interface and the dissolution rate therefore increases again with time till it attains the equilibrium values shown. The surface layer structure in this region appears to be different from the one in the active portion and the electrode seems to be covered by an insoluble oxide, the outer surface of which is converted into the soluble variety. This picture is similar to

that suggested by Huber,[5] and is further supported by our results in N/10 saturated solutions, for which the equilibrium rates in this, " passive region " become —ve again (see Fig. 8), showing that under these conditions, hydrogen evolution or zinc deposition are possible on the coherent oxide layers. This is further discussed under ' dilute solutions '.

On further increasing the voltage, in all solutions current-time transients are obtained (not shown) in which the rates are initially high and then decrease with time to equilibrium values showing that in this region, the thickness of the oxide layer increases with voltage. However, in N/10 solutions, the equilibrium currents eventually become —ve for a short-voltage region.

When the potential is increased further, the V–I curves show various complexities. It is not certain how far these minor complications are due to the small deviations of the measured rates from the true equilibrium rates. The basic behaviour in all solutions is however similar, the rate of dissolution remaining relatively constant over a considerable voltage range. It would appear that the behaviour of the electrode in this potential region is governed by a fixed rate of dissolution of the oxide in the electrolyte, the potential increments merely increasing the thickness of the layer so as to maintain the field strength required to continue the necessary cation transport, by high field conduction,[6–8] for the fixed rate of dissolution.

The fact that the behaviour of the electrolyte in this ' passive ' region is controlled by high field conduction in conjunction with a fixed rate of dissolution is confirmed by the time-rate transient in Figs. 9 and 10. It is seen that in dropping the voltage from + 1·8 to 0 V. the current cuts off in every case. Initial small —ve currents are probably due to the discharge of space charges in the oxide layers.[9–11] Even though the voltage across the layer is only halved, the rate initially becomes 0. This can only be explained by assuming that a decrease of the field strength reduces the lowering of the energy barrier, between interstitial diffusion positions sufficiently to prevent cation transport at this temperature. As the layer however dissolves the field strength again increases and the rate approaches its equilibrium value.

It must however be pointed out that the position is not so simple, as the time-rate transients, particularly in concentrated solutions (Fig. 10), show marked maxima which indicate that the surface layers somehow temporarily become more soluble and the rates then fall off. It could be suggested that this might be due to the ageing of the surface oxides which become less soluble with time. But this explanation does not seem to be valid in these cases as the layers had already been in the solution for about

30–40 mins. when these maxima are observed. Moreover the maxima extend only to a relatively short time which could not be supposed to age or change the surface oxides. In 6 N KOH the maximum rate on dropping the potential is even higher than the rate at the same potential while going up the potential range stepwise. This also shows that the dissolution is not a simple process.

Oxygen Evolution.—Beyond about 1·5 V. oxygen evolution becomes the predominant reaction, the current rate depending on the solution, but steeply rising in all cases and under all conditions. Generally speaking the rates are higher and rise more steeply for stirred solutions and for solution without zincate than for unstirred or solutions saturated with zincate.

Dilute Solutions

In N/10 KOH saturated with ZnO and in all N/100 solutions the V–I plots are markedly dependent on the time taken to reach various potentials and therefore the currents after 45 secs. at any potential cannot be taken as the equilibrium rates. This fact can be seen by comparing the Figs. 7 and 8. It was found that in order to obtain true equilibrium rates it was necessary to maintain the potential fixed at each 0·1 V. step for at least 30 mins. Such a procedure can only be justified and adopted if fresh electrodes are used and separate experiments made at each 0·1 V. step, for pronounced ageing effects may be observed if the surface layers are kept in the electrolyte for long periods (see below).

An alternative procedure found suitable was first to raise the potentials sufficiently and then drop them to lower values. This was based on the inference that the layer thickness increases with voltage, since when the voltage is dropped, the current first cuts off and then gradually increases, presumably till the equilibrium thickness and rates are attained. This method may therefore be used to construct the equilibrium V–I curves. The data so obtained are shown in Fig. 6 and curves are given for voltage drops from + 1·8 and + 1·0 V. to various lower values. These differ from each other only in a narrow region. If the voltage is dropped from + 0·5 or from 0 V. to values in between these potentials and − 1·3 V., the currents obtained after ½ hour lie between the curves marked.

The only difference between these final rates lies in the age of the oxide layer and it is evident that in the second I–V plateau region, determined by the rate of zincate ion formation, the age of the oxide affects the rate of dissolution.

The basic behaviour of the equilibrium curves, obtained by both these methods, is similar. Oxide begins to form above − 1·3 V. as can be seen

from current-time transients, and the layer continues to thicken with increasing voltage.

At potentials −ve to − 0·7 V. (in Fig. 6) the final rate on the completed oxide deposits is negative and remains constant for a considerable voltage interval. This may be explained by assuming that the oxide/solution interface potential is constant thereby maintaining a constant rate of hydrogen evolution. It appears that the fixed rate of attack and zincate formation determines the field strength, necessary to maintain a constant current. The thickness of the deposit should therefore be proportional to the applied voltage. Preliminary measurements of the quantity of the oxide on the surface appear to confirm this.

The constancy of the field strength automatically fixes the magnitude of the charge on the solution-side of the electrolytic condensor, consisting of OH^- ions. This, in turn, keeps the Helmholtz potential, on the oxide/solution interface, constant. Thus, the reason for a constant hydrogen evolution rate may easily be seen. For very thin films, however, the rate of H_2 evolution increases rapidly. The reason for this is not clear but it is possible that at very −ve potentials there may be repulsion between zinc and OH^- ions which becomes effective through thin films, thereby making the Helmholtz potential less + ve and increasing the rate of hydrogen evolution. This view agrees with Antropov's theory of ϕ potentials.

This possibility of discharge of hydrogen on ZnO indicates the difficulty of accepting the coulometric estimates of oxide thickness, as obtained by some workers. Our experiments, on the reduction of oxide layers, also show that the rate of hydrogen evolution is often comparable to the electrochemical reduction of ZnO. Similarly, it may also be foreseen that zinc from zincate solutions could be deposited on the oxide layers, which would render such deposits to be of poor quality. This agrees very well with our observations and discussion in the previous papers.[1, 12]

As the potential is further made more +ve to − 0·7 V. there is a sharp transition from the −ve to a +ve current plateau (Fig. 6). This shows that when the oxide thickness exceeds a certain value, the transition probability of the electrons is so reduced that H_2 evolution ceases thereby reversing the currents. The current-time integrals indicate that the layers at this point are roughly 200 Å thick. It is therefore possible that in the −ve current plateau, where layers are much thinner, electron-transfer occurs by way of " tunnel effect ".

Also, it appears that the ϕ or zero-charge (null) potential of zinc lies in this region and hence it may be expected that as the potential changes in the

vicinity of $-0{\cdot}7$ V., the nature and charge of the Helmholtz layer or the orientation of the adsorbed dipoles on zinc changes. This would also account for the sudden change in the sign of the current as the potential is further made more + ve.

In the +ve current plateau region between $-0{\cdot}6$ and $+1{\cdot}0$ V., the reaction on the oxide/solution interface appears to be zincate formation. The field strength must therefore again remain constant to maintain the required cation transfer. But, in this case, as distinct from the case of Ta and Al, the electrolytic condensor does not infinitely increase in thickness. On the other hand very soon a breakdown of the field occurs and oxygen evolution starts at about $1{\cdot}0$ V., leading to a third current plateau region in which oxygen evolution remains constant with increasing potential. The reason for such an early oxygen evolution may be that a large space-charge is set up in zinc oxide. This could lead to a rapid alteration of the Helmholtz potential with increasing film-thickness and thereby enable oxygen evolution. This view is supported by the fact that the relatively thicker layers of ZnO are often found, at this stage to be black and therefore contain a large quantity of interstitial zinc ions,[5] whereas Ta and Al surface layers are not so.

Finally, on increasing the voltage, the current rate is once again found to rise suddenly and sharply. This corresponds with vigorous oxygen evolution but the mechanism of this change is not yet clear.

Before this final rapid increase in current, a constant rate of oxygen evolution, similar to that observed in N/100 solutions, is found also in N/10 solutions. But, in more concentrated solutions only a single plateau is observed, the overall current initially decreasing with increasing voltage, when oxygen evolution sets in.

If the 25 mV. potential steps are used to get a more detailed plot in the region $-1{\cdot}3$ to $-0{\cdot}8$ V. in N/10 KOH saturated with ZnO, a − ve current can be observed (Fig. 8) after the active portions of the V–I curves while in more concentrated solutions a + ve current is observed in this region; over a short voltage interval and with increasing voltage the currents rise to a more +ve constant value. This, therefore, suggests that probably in all solutions and particularly in dilute solutions there may be hydrogen evolution in this post-active region but as the actual currents measured are merely the differences between hydrogen evolution and zincate formation rates, the observed signs are sometimes +ve and sometimes −ve depending on the potential steps, the concentration of the solution and the procedure of measurements. The increasing +ve rate after the active region is therefore to be attributed to the gradual cessation of electron transport through thickening films,

The idea of superposition of ' mixed ' currents in which some points ac as anode and some as cathode on one and the same electrode thereby producing both anodic and cathodic currents to different degrees is well known and has already been postulated by many authors including Laidler, Glasstone and Eyring,[13] Uhlig,[14] Stern,[15] Antropov,[16] etc. Moreover, if the I–V plot for zinc in N/10 KOH, saturated with ZnO, as shown in Fig. 8 is redrawn on a larger and non-logarithmic scale, it will be seen (Fig. 8 A) that the extent of —ve current through zinc is really very small, *i.e.*, only about 30 μA which could be easily accounted for if under the above conditions the electron flow somehow slightly predominates over cation transport. Also it should be remembered that Gilbert,[17] Evans[18] and others have shown that the semiconducting zinc oxide layers can suddenly become anodic or cathodic even when dipped in water, by merely a change of temperature.

Also, it is known that for zinc, pH plays an important role in hydrogen evolution for which the hydrogen-ion-discharge is the rate determining step. This may account for these complicating observations only in the case of dilute solutions, where the $(OH)^-$ ion is liable to tremendous changes at the electrode surface.

An interesting phenomenon is observed in unstirred N/100 solutions in the oxygen evolution region (Fig. 7). With increasing voltage beyond 2·0 V. the current rises to values above these in stirrred solutions. On suddenly dropping the voltage to 0 V. the current drops to about 1·4 mA which is about 10^2 times larger than the corresponding current in stirred solutions. This breakdown of the passivating films in unstirred solutions must be due to the relative increase of zincate ion concentration, with respect to (OH^-), when OH^- ions are removed at a rate of the order of limiting rate of diffusion. Similar film breakdowns were also actually observed at lower potentials by the addition of SO_4^{--} ions. This strong autocatalytic effect of the zincate ions is in agreement with our previous observations on the equilibrium rates at lower potentials and also conforms to the theory of strong adsorption of anions at potentials $\gg$ null potential.

CONCLUSIONS

These potentiostatic observations fully explain and account for the previous results obtained under constant current conditions.[1] The main difference is that the constant current methods only reveal two stages in the polarisation of zinc, *i.e.*, either active or passive but the V–I curves obtained by the constant potential method clearly show that there are various intermediate stages which may be jumped over, if a constant current is enforced,

while going from active to passive state, but which must be passed when going back from passive to the active region as this involves the dissolution and consequent thinning of the surface layers. This accounts for the fact that electrodes were not found to become active immediately on reducing the current density, after passivation had once been achieved.

The point where the current starts to fall in the active region of the V–I curves may be taken to correspond to the stage of sudden passivation and consequent potential jump to a much higher but variable voltage, required for the appropriate rate of oxygen evolution, under the conditions, of enforced constant current.

The lengths of the maximum current plateau obtained in the V–I curves tend to indicate that a certain thickness and condition of surface layers is necessary before the current starts to drop. This is analogous to the fact that a minimum duration of polarisation at any fixed current density was necessary to passivate the electrode. Also, if a current greater than the maximum rate is applied, the electrode would not pass through any active portion at all, but would immediately jump on to oxygen evolution.

The indefinite rest potential of zinc electrodes in dilute solutions is explained by the fact that hydrogen evolution is possible on the coherent oxide films. This enables the open-circuit potential to set itself to values at which the zinc corrosion rate in the solution is equal to the rate of hydrogen evolution. The apparent arrests obtained in the decay curves and on sudden cathodic polarization of passive electrodes are also readily explained in this manner.

Acknowledgement

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PULSE SPREAD IN PROPORTIONAL COUNTERS

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1. Introduction

Proportional counters are being extensively employed for measuring energies of nuclear particles. In an ideal proportional counter, the pulse height would be directly proportional to the energy of the particle, when the energy per ion pair production is constant, or to the total amount of ionization produced by the particle in the sensitive volume of the counter. In practice, it is observed that particle tracks, giving rise to the same amount of ionization in the sensitive volume of the counter, do not give rise to pulses of the same height. This behaviour has been attributed to space-charge effects, electron attachment and end effects. Other possible causes are inequalities in the diameter of the wire and the presence of dust particles on the wire.

Of particular interest is the study of the influence of the departure from co-axial cylindrical geometry on the spread of pulse height. Although theoretical treatment of the effect of eccentricity of the central wire (Rossi and Staub, 1949; Venkatasubramanian and Krishnan, 1957) has been given, no experimental verification of the theory seems to have been carried out with proportional counters. The present investigation describes results of such a study.

2. Experimental Technique

In all, three different counter geometries were studied:

(*A*) *Eccentric Wire Counter.*—The counter was made of a cylindrical copper cathode, 3 cm. in diameter and 6·5 cm. long, with a 3 mil. tungsten wire stretched along the length of the cylinder, 3 mm. away from the axis.

(*B*) *Circular Counter.*—A circular counter, made of copper, 4·5 cm. in diameter and 2 cm. deep, was employed. A 3 mil. tungsten wire was stretched along a diameter,

(*C*) *Loop Counter.*—A counter, made of brass, 2·5 cm. in diameter and 2·2 cm. deep, was used. A loop of diameter 8 mm. made of a 3 mil. tungsten wire was supported along a diametral plane.

All the three counters were filled with tank argon to a pressure of 10 cm. The usual precautions in the assembly of the counter were observed, the central wire being cleaned and examined to be free of kinks and dust particles. The cathode was also thoroughly cleaned.

The source in each case was a thin polonium coated foil. The α particles from this source were collimated by a thick cover plate, with a fine aperture (1 mm.).

High voltage to the counters was applied from a regulated power supply. The pulses were fed to a linear amplifier, with a flat frequency response up to 500 Kc. and a maximum mid-band gain of 16,000. From the magnitude of the output pulses, the amplifier gain setting and the calculated ionization of the α track, the gas amplification in each case was computed and found to be about 50 in all the three cases.

The amplified pulses were displayed on a cathode ray oscilloscope screen. The oscilloscope sweep was triggered by the pulse. The pulses were photographed on a stationary plate (Hofstadter and McIntyre, 1950). The spread in the intensity gave directly a measure of the spread in pulse height. Intensities were measured by means of a microphotometer, and plotted as a function of the relative pulse heights. The half-width of pulse spread is obtained from the resulting differential curve.

3. Results and Discussion

The main features of the investigation are presented in the three representative graphs, Figs. 1, 2 and 4. The half-width of the pulse height distribution, defined as the interval which contains 50% of all the pulses counted, is obtained from these curves.

(*A*) *Eccentric Wire Counter.*—The effect of a finite eccentricity of the wire has been studied theoretically by Venkatasubramanian and Krishnan (1957). They give, for particle tracks coming from either side along the line of centres, the expressions for the gas amplification factors. For a counter of two cylinders of radii a and $b > a$ with their axes parallel and their centres at a distance d,

$$\log A_1 = \left[\frac{\alpha V}{\theta - \phi}\right]^{1/2} \left[(r_1^{1/2} - a^{1/2}) + \frac{p}{3a^2}(r_1^{3/2} - a^{3/2})\right]$$

and

$$\log A_2 = \left[\frac{\alpha V}{\theta - \phi}\right]^{1/2} \left[(r_2^{1/2} - a^{1/2}) - \frac{p}{3a^2}(r_2^{3/2} - a^{3/2})\right]$$

where,

$$\frac{p}{a} = e^{-\theta}; \quad \cosh\theta = \frac{b^2 - a^2 - d^2}{2ad}$$

$$\frac{q}{b} = e^{-\phi}; \quad \cosh\phi = \frac{b^2 - a^2 + d^2}{2bd}.$$

Here, r_1 and r_2 are the critical radii for the onset of Townsend avalanches for particle tracks along the line of centres. V is the applied voltage and α is the first Townsend coefficient.

For the counter dimensions stated above, we have

$$\frac{A_1}{A_2} = 1{\cdot}40$$

where A_1 and A_2 are the gas amplification factors for particle tracks coming from either side, along the line of centres. The curve, in Fig. 1, gives the half-width as of the order of 25%, which is in fairly good agreement with the theoretical considerations.

(*B*) *Circular Counter.*—Moving the source to different positions in the counter, the spread in pulse height is found in this case to be of the order of 30% (Fig. 2). While this spread is appreciable, it represents an upper limit to the spread resulting from a departure from co-axial cylindrical geometry.

(*C*) *Loop Counter.*—The loop counter presents a new type of counter geometry which is being employed in a number of flow type proportional counters (Price, 1958). Hence, a study of the spread in such a geometry is useful.

In this case, one has to distinguish between two extreme types of particle tracks, in the plane of the loop and perpendicular to the plane. A theoretical expression for the fields in the two directions can be derived as follows. It is found that they are equal to the first order, suggesting that there should be no appreciable spread.

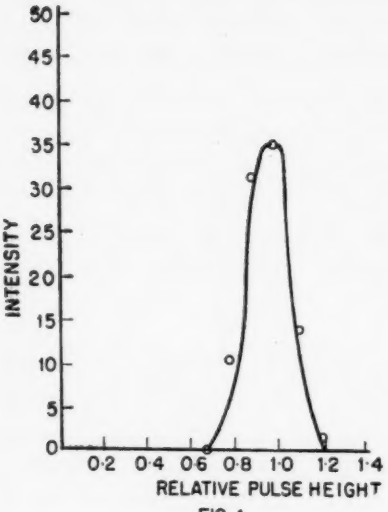

FIG. 1

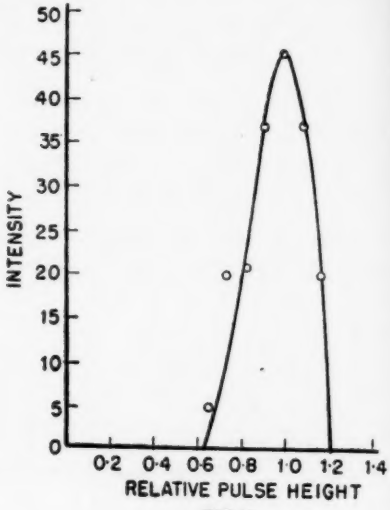

FIG. 2

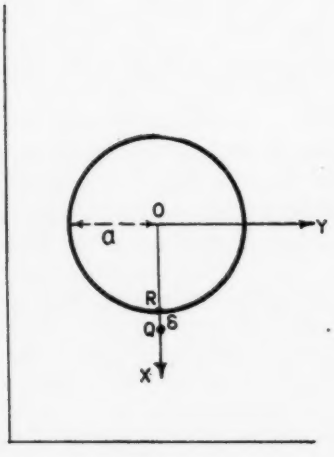

FIG. 3

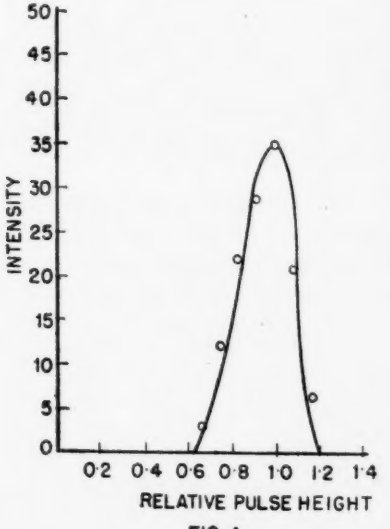

FIG. 4

In Fig. 3, the loop is in the plane of the paper, with the z-axis $\perp r$ to this plane at 0. For a point P whose co-ordinates are (ρ, z) in the $x - z$ plane, the potential function can be written as

$$\Phi_P = \frac{2\lambda}{[(\rho + a)^2 + z^2]^{1/2}} \cdot \int_0^{\pi/2} \frac{d\beta}{[1 - k^2 \sin^2 \beta]^{1/2}}$$

$$= \frac{2\lambda}{[(\rho + a)^2 + z^2]^{1/2}} \cdot \mathrm{K}(k)$$

where $\mathrm{K}(k)$ is an elliptic integral of the first kind. Expanding this function, we get

$$\Phi_P = \frac{\lambda}{a} \cdot ln\left(\frac{4}{k'}\right)$$

where

$$k'^2 = 1 - \left[\frac{4\rho a}{(\rho + a)^2 + z^2}\right].$$

The fields in the plane of the loop and perpendicular to the plane can now be obtained by differentiation with respect to x and z respectively. We get,

$$\mathrm{E}_x = \frac{\lambda}{a\delta}$$

and

$$\mathrm{E}_z = \frac{\lambda}{az}$$

for $\delta \ll a$, which is the case, as gas multiplication takes place only in a very small region around the central wire. If δ and z are the distances in the directions OX and OZ, at which gas multiplication begins, to the first order, $\mathrm{E}_x = \mathrm{E}_z$ (for $\delta = z$) and there is no spread in gas amplification. The experimental curve gives the spread as being of the order of 30% (Fig. 4).

The fact that spreads of the order of 30% are obtained may be attributed to several factors, such as non-uniformity of the wire. In fact, an ordinary cylindrical type of proportional counter, constructed with the normal precautions and operated under the same conditions, yielded pulse spreads of the order of 20% with the same polonium source. As no precautions have been taken to minimize these effects, the resultant spreads are not of an alarming nature. Where detection of groups of particles of appreciably different energy is the main criterion, and not absolute energy determinations, these spreads are quite acceptable. It is thus seen that counters differing widely

from the usual co-axial cylindrical geometry can be successfully operated in the proportional region.

4. SUMMARY

An experimental study of the spread in pulse height in proportional counters with different counter geometries is undertaken. It is shown that the spread is of the order of 30%. This spread due to deviation from cylindrical geometry does not present a serious difficulty for discrimination of particles of sufficiently different energies.

5. ACKNOWLEDGEMENT

I thank Professor R. S. Krishnan for guidance. I also thank Dr. V. S. Venkatasubramanian for suggestions and helpful discussions.

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HETEROCYCLIC COMPOUNDS

Part XIV.* Synthetic Experiments in the Pyrido-(1, 2 *a*)-Pyrimidone Series

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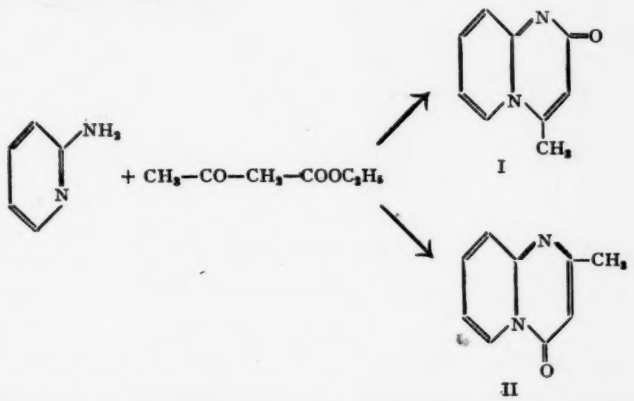
The formation of a pyrido-(1, 2 *a*)-pyrimidone from ethyl acetoacetate and 2-amino-pyridine was studied by several workers[1] under different conditions. The product was first formulated as 4-methyl-2H-pyrido-(1, 2 *a*)-pyrimidin-2-one (I) and later as 2-methyl-4H-pyrido-(1, 2 *a*)-pyrimidin-4-one (II). The latter structure was confirmed by Adams *et al.*[2] by the studies of ultraviolet absorption curves of several pyrido-(1, 2 *a*)-pyrimidones and by providing unequivocal chemical evidence. The synthesis of the isomer (I) has not yet been effected.



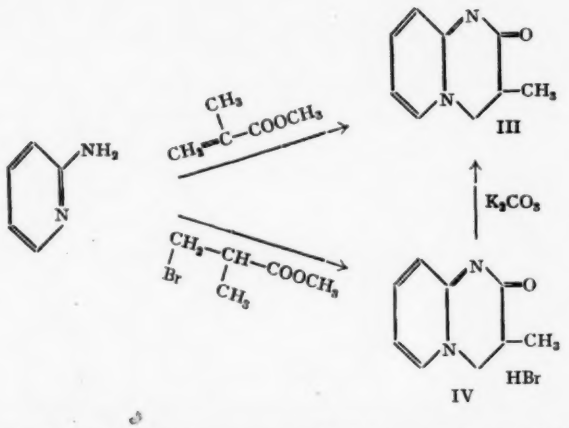
In continuation of work already reported from this laboratory,[3] it was proposed to synthesise the compound (I) or its 3, 4-dihydro derivative by the reaction of homologues of acrylic ester or β-bromo-propionic ester with 2-amino-pyridine and other methyl-substituted 2-amino-pyridines. The condensation of 2-amino-pyridine or methyl-2-amino-pyridine with ethyl β-bromo-butyrate or β-bromo-butyric acid was attempted according to the

* Part XIII, *Proceedings*, 1958, Vol. XLVII, No. 4, Sec. A, p. 244.

method of Adams.[2] Addition of ethyl crotonate (or crotonic acid) to 2-amino-pyridine (and methyl-2-amino-pyridines) to form the cyclised base (I) was also attempted by Adams' method. In each case, no reaction took place and most of the reactants were recovered unchanged.

2-Amino-pyridine was condensed with α-methylmethacrylate by heating the reactants on the water-bath in the presence of little tertiary-butyl catechol as the polymerisation inhibitor. The expected base, 3-methyl-3, 4-dihydro-2H-pyrido-(1, 2 *a*)-pyrimidine-2-one (III) was obtained in fairly good yields.

The hydrobromide (IV) of the above base was also obtained by heating 2-amino-pyridine with methyl β-bromo-isobutyrate in absolute chloroform for twenty-five hours. The ultraviolet spectrum of (IV) was compared with the known pyrido-(1, 2 *a*)-pyrimidin-2-ones (see Fig. 1). The similarity of the spectrum to that of the known compounds lends additional evidence to the structure.



However, when the reaction was applied to methyl-substituted 2-amino-pyridines, the expected condensation products could not be obtained. When the reactants were refluxed for eight hours in chloroform, the hydrobromides of the pyridine-amines were precipitated. This action is in sharp contrast to simple 2-amino-pyridine which showed little tendency to act as a dehalogenating agent. Drake and McElvain[4] observed differences in the nature of the reactivity of bromo-esters towards piperidine, the difference being related to the position of the bromine atom. In this investigation it is found that the same bromo-ester reacts differently when passing from 2-amino-pyridine to methyl 2-amino-pyridines.

The difference in behaviour now reported between 2-amino-pyridine and four methyl-substituted 2-amino-pyridines towards β-bromo-isobutyric ester is probably be due to greater basicity of methyl-substituted 2-amino-pyridines. Brown *et al.*[5] and Bruehlman and co-workers[6] have reported similar observations. It is known that the basicity of pyridine molecule is increased by the introduction of methyl group, the inductive as well as hyper-conjugative effect of the methyl group being responsible.

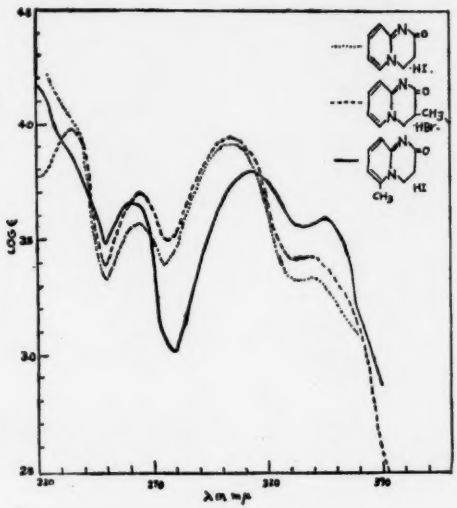


FIG. 1

EXPERIMENTAL

Condensation of ethyl β-bromo-butyrate and 2-amino-pyridine

Ethyl β-bromo-butyrate was prepared according to the method of Johanson.[7] 2-amino-pyridine (1·8 gm.) and ethyl β-bromo-butyrate (3·9 gm.) were refluxed for twenty-four hours in 20 ml. of chloroform. No solid separated.

The chloroform layer was successively extracted with water. The base, obtained on evaporation of acqueous extract, was characterised as 2-amino-pyridine by conversion into the picrate, m.p. 216–17°. Most of the above ester was recovered from the chloroform layer.

The substitution of β-bromo-butyric acid instead of the ester did not effect the condensation. Methyl-2-amino-pyridines also did not condense with the above acid or ester.

Condensation of ethyl crotonate and 2-amino-pyridine

Ethyl crotonate (2·8 gm.), 2-amino-pyridine (2·3 gm.) and of tertiary-butyl catechol (0·05 gm.) were heated on the water-bath for twelve hours. Working up the product in the same way as above, it was found that the reaction did not take place at all.

3-methyl-3, 4-dihydro-2H-pyrido-(1, 2 a)-pyrimidin-2-one

2-amino-pyridine (4·7 gm.), α-Methylmethacrylate (5 gm.) and of tertiary-butyl catechol (0·1 gm.) were heated on the water-bath for twelve hours without any solvent. The dark solution was kept in the ice-chest for two days. Small flowery crystals separated. It was triturated with 10 ml. of benzene and filtered. The solid was dissolved in 10 ml. of chloroform, boiled with charcoal and filtered. The solution upon dilution with light petrol (40–60°) yielded white powdery substance of m.p. 195–96°. Repeated crystallisation from chloroform-petrol mixture raised the m.p. to 199–200°.

Found: C, 66·25; H, 6·05; Calculated for $C_9H_{10}N_2O$. C, 66·67; H, 6·17.

The picrate of the base was prepared in the usual manner. The yellow picrate was crystallised from ethanol, m.p. 181–82°.

Found: C, 46·36; H, 3·6; Calculated for $C_9H_{10}N_2O.C_6H_3N_3O_7$. C, 46·04; H, 3·33.

It was observed that the mother liquor, after removal of the crude base, when kept in the ice-chest for a long time deposited crystals which were identified as 2-amino-pyridine.

The hydrobromide of 3-methyl-3, 4-dihydro-2H-pyrido-(1, 2 a)-pyrimidin-2-one

Methyl β-bromo-isobutyrate was prepared by the method of Clemo and Melrose.[8] A solution of 2-amino-pyridine (1·98 gm.) and β-bromo-isobutyric ester (3·6 gm.) in 30 ml. of dry chloroform was heated under reflux for twenty-four hours. Solid separated after 12 hours of refluxing. The solid was filtered and dissolved in minimum amount of absolute ethanol and completely precipitated by the addition of absolute ether. 2·4 gm. of the hydrobromide of m.p. 293–95° was obtained. An analytical sample after two recrystallisations from ethanol-ether mixture melted at 300° (decomp.).

Found: C, 44·42; H, 4·7; N, 11·1; Calculated for $C_9H_{10}N_2O.HBr$. C, 44·42; H, 4·5; N, 11·5. The u.v. spectrum was taken in 95% ethanol.

	$\lambda_{max.}$ in mμ	$\epsilon_{max.}$
3-methyl-3, 4-dihydro-2H-pyrido-(1, 2 *a*)-pyrimidin-2-one hydrobromide	235	9815
	265	4955
	305	8974
	340	2664
3, 4-dihydro-2H-pyrido-(1, 2 *a*)-pyrimidin-2-one hydroiodide[3]	265	3722
	305	8664
	340	2175
6-methyl-3, 4-dihydro-2H-pyrido-(1, 2 *a*)-pyrimidin-2 one hydroiodide[3] ..	260	4580
	315	6360
	345	3944

The picrate prepared from the hydrobromide had m.p. 181–82° undepressed by authentic specimen prepared from the base. The free base, obtained from the hydrobromide, had m.p. 195–97°.

Condensation of 5-methyl-2-amino-pyridine and methyl β-bromo-isobutyrate

5-methyl-2-amino-pyridine (2·1 gm.) and methyl β-bromo-isobutyrate (3. 6 gm.) were refluxed for 12 hours in 25 ml. of chloroform. A strong odour of α-methylmethacrylate was noticed after six hours. The precipitated solid (3 gm.) was crystallised from absolute methanol-ether mixture, m.p. 170–72°. Two more recrystallisations from the same solvent increased the m.p. to 175–76°.

Found: C, 38·2; H, 5·2; $C_6H_8N_2HBr$ requires C, 38·05% and H, 4·7%.

The picrate of 5-methyl-2-amino-pyridine was prepared in the usual manner. On crystallisation from isopropyl alcohol, it separated as yellow fluffy mass, m.p. 249–50°.

Found: N, 20·75; Calculated for $C_6H_5N_2.C_6H_3N_3O_7$. N, 20·77. The picrate from the hydrobromide melted at 249° and the mixed m.p. of the two picrates remained constant.

Condensation of 4-methyl-2-amino-pyridine (2·1 gm.) and methyl β-bromo-isobutyrate (3·6 gm.) in the same manner yielded 3 gm. of the hydrobromide. The hydrobromide though it melted sharply at 162–63°, was hygroscopic and could not be obtained analytically pure. The m.p. of yellow picrate (from acetic acid) was 227° and remained constant upon admixture with pure sample.

In the case of 3-methyl-2-amino-pyridine, the hydrobromide obtained melted at 153–55°, but was also too hygroscopic to work with. The picrate

from the salt melted at 229° (yellow prisms from alcohol). The mixed m.p. of the picrates remained the same.

3·5 gm. of the hydrobromide was obtained from the condensation 2·1 gm. of 6-methyl-2-amino-pyridine and 3·6 gm. of methyl β-bromo-isobutyrate. The HBr salt had m.p. 142°. After three recrystallisations from ethanol-ether mixture, it melted at 149°. The reported m.p. in the literature[9] is 149–50°. The picrate melted at 202° and was identical with pure specimen.

SUMMARY

Synthesis of 3-methyl-3, 4-dihydro-2H-pyrido-(1, 2 *a*)-pyrimidin-2-one is reported. Methyl β-bromo-isobutyrate on reacting with methyl-substituted 2-amino-pyridines underwent dehalogenation with the production of unsaturated compound.

ACKNOWLEDGEMENT

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POLAROGRAPHIC BEHAVIOUR OF ORGANIC IODOCOMPOUNDS

Part III. *o*-Iodobenzoic Acid.

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Introduction

The investigations on iodobenzene[1] and 2-iodonaphthalene[2] have brought to light several interesting features regarding the variation of the diffusion current with changes in the concentrations of the organic solvent. This work has therefore been extended to include iodobenzoic acids, since their reduction is similar to the compounds already studied and in addition their reduction is pH dependent. As in the case of iodobenzene some workers[3-5] have used arbitrarily chosen concentrations of organic solvent for investigating their polarographic behaviour while Elving and Hilton[6] have studied only in the aqueous medium. In the present work, the effect of different concentrations of ethanol, dioxane and acetone on the polarographic characteristics and diffusion coefficients of *o*-iodobenzoic acid at different acidities are presented.

Experimental

The polarographic experimental procedure is the same as described previously.[1] The values of '*m*' of the capillaries used are 1·227 and 1·150 mg. per second. The droptime '*t*' has been adjusted to 5 seconds a drop in normal potassium chloride solution. 0·5 M lithium chloride is employed as the indifferent electrolyte. The acidity of the solutions has been varied by the use of Walpole's buffers[7] for the acid region (pH 3·3 to 5·5), sodium acetate for pH 7, Sorenson's buffer[7] for pH 9 and Kolthoff's buffer[7] for pH 11. The concentrations of the reagents were such that no precipitation occurred when the different reagents are mixed. The pH is measured using a Beckman pH meter and they refer to the values in the aqueous medium. The polarograms have been recorded at 30° ± 0·1° C. The diffusion coefficients have also been determined at the same temperature using the diaphragm cell

technique described previously.[1] The cell constant has been found to be 0·5872 units per second.

o-Iodobenzoic acid is prepared by diazotisation of anthralinic acid and subsequent conversion to the iodocompound.[8]

It has been found that in presence of large concentrations of dioxane or ethanol (75%) or *o*-iodobenzoic acid (> 2 mM), a kink appears on the C–V curve. However, the kink can be eliminated by gelatin (0·001 to 0·002%). The presence of these kinks does not materially affect the diffusion current constant. The addition of gelatin did not have any noticeable effect on the diffusion current.

RESULTS

1. *Effect of concentration of organic solvent on the diffusion current constant, half-wave potential and* $E_{\frac{1}{4}}$–$E_{\frac{1}{4}}$ *of* o-*iodobenzoic acid at different acidities.*—A few typical polarograms are given in Figs. 1, 2, 3 and 4. The results of analysis of the polarographic waves obtained under different conditions are presented in Table I.

An examination of Table I indicates that the diffusion current constant decreases with an increase in the concentration of the organic solvent. This is in contrast to the behaviour of iodobenzene[1] where an increase has been noticed. The magnitude of the variation, however, is smaller in the present system. At low pH values, where low concentrations of organic solvents are employed, either no wave or ill-defined wave appears due to interference from hydrogen discharge. The half-wave potential shifts to more negative values both when there is an increase in the pH of the solution at constant concentration of the organic solvent and when there is an increase in the concentration of the organic solvent at constant pH. The value of $E_{\frac{1}{4}}$–$E_{\frac{1}{4}}$ is of the order of 0·1 V. in all the cases. As the values of $E_{\frac{1}{4}}$–$E_{\frac{1}{4}}$ do not deviate very much from 0·1 V., direct comparison of the half-wave potentials can be made.

2. *Influence of the solvent on the diffusion coefficient of* o-*iodobenzoic acid.*—It can be seen from Table I that above pH 5·5, the height of the polarographic wave is dependent mostly upon the concentration of the organic solvent and not so much upon the pH of the solution. Hence one pH, namely 11, has been chosen for investigating the relationship between the diffusion coefficient and the diffusion current constants at different cencentrations of the organic solvent. The diffusion coefficients determined by employing the diaphragm cell and those derived from viscosity data are given in Table II. For the calculation of the diffusion coefficient by the viscocity

TABLE I

Effect of concentration of organic solvent on the polarographic behaviour of o-iodobenzoic acid at different acidities

pH	% solvent	Ethanol: Diffusion current constant	Ethanol: $E_{\frac{1}{2}}$ *vs.* S.C.E. (volt)	Dioxane: Diffusion current constant	Dioxane: $E_{\frac{1}{2}}$ *vs.* S.C.E. (volt)	Acetone: Diffusion current constant	Acetone: $E_{\frac{1}{2}}$ *vs.* S.C.E. (volt)
		No wave below 25% of organic solvent					
3·3	25	2·34	−1·143	2·64	−1·231	3·12	−1·310
	50	2·25	−1·250	2·23	−1·526	2·98	−1·583
	75	2·23	−1·310	2·09	−1·591	2·97	−1·620
	98	2·13	−1·320	..	..	..	..
		No wave below 25% of organic solvent					
5·5	25	2·69	−1·142	2·34	−1·490	3·30	−1·250
	50	2·36	−1·442	2·25	−1·550	3·27	−1·580
	75	2·19	−1·600	2·23	−1·610	3·20	−1·621
	98	2·01	−1·618	..	..	..	..
7·0	0	3·93	−1·563	3·93	−1·563	3·93	−1·563
	10	3·01	−1·563	3·23	−1·568	3·86	−1·572
	25	2·87	−1·567	2·65	−1·573	3·61	−1·620
	50	2·33	−1·581	2·39	−1·580	3·50	−1·641
	75	2·23	−1·603*	2·24	−1·620*	3·49	−1·650
	98	2·19	−1·625*	..	..	..	..
9·0	0	3·80	−1·564	3·80	−1·564	3·80	−1·564
	10	3·46	−1·593	2·99	−1·570	3·69	−1·573
	25	2·99	−1·598	2·97	−1·603	3·21	−1·578
	50	2·30	−1·602	2·47	−1·610	3·21	−1·618
	75	2·28	−1·610*	2·14	−1·620*	3·11	−1·625
	98	2·25	−1·622*	..	..	..	..
11·0	0	3·97	−1·563	3·97	−1·563	3·97	−1·563
	10	3·46	−1·587	3·94	−1·587	3·80	−1·573
	25	2·99	−1·600	3·14	−1·588	3·27	−1·580
	50	2·29	−1·613	2·49	−1·610	3·25	−1·610
	75	2·27	−1·621*	2·01	−1·620*	3·22	−1·623
	98	2·20	−1·624*	..	..	..	..

* 0·001% gelatin has been included in the base solution.

method, the value for the molar volume of *o*-iodobenzoic acid has been taken as 161·6. Equivalent conductivity data gives a value of $9·39 \times 10^{-6}$ sq. cm.

per second for the diffusion coefficient at 30° C.[9] The details of calculation are the same as described previously.[1]

TABLE II

Diffusion coefficient of o-*iodobenzoic acid at different concentrations of organic solvent using the diaphragm cell method and the viscosity method*

Solvent	% by volume of solvent	η of the base solution (centipoises)	$D \times 10^6$ (sq. cm. per sec.) diaphragm cell method	$D \times 10^6$ (sq. cm. per sec.) viscosity method
Ethanol ..	0	0·867	11·91	6·37
	10	1·136	9·49	4·86
	25	1·651	5·94	3·35
	50	2·005	3·66	2·76
	75	2·201	3·55	2·51
	98	2·340	3·40	2·36
Dioxane ..	10	1·020	11·67	5·42
	25	1·420	6·49	3·89
	50	1·970	4·81	2·80
	75	2·680	2·96	2·06
Acetone ..	10	1·013	11·42	5·46
	25	1·209	7·97	4·57
	50	1·308	6·95	4·23
	75	1·392	6·87	3·97

It is clear from the table that the diffusion coefficients by the diaphragm cell method differ greatly from those derived from viscosity data at all concentrations of the three organic solvents employed. It is interesting to note that this observation is at variance with that noticed in the case of iodobenzene,[1] where the diffusion coefficient by the diaphragm cell method increased with an increase in the concentration of the organic solvent, while those derived from viscosity data decrease.

3. *Effect of concentration of* o-*iodobenzoic acid on the diffusion current constant.*—Proportionality between the diffusion current and the concentration of *o*-iodobenzoic acid has been tested in base solutions containing 50% of the organic solvent at pH 11. As has already been pointed out a kink appears on the C–V curves when the concentration of *o*-iodobenzoic acid is greater than 2 millimolar. 0·002% gelatin has been incorporated in these

base solutions to eliminate the kink. In Table III are presented the values of the diffusion current constants at different concentrations of *o*-iodobenzoic acid.

TABLE III

Effect of concentration of o-*iodobenzoic acid on the diffusion current constant at pH* 11

50% ethanol (by volume) $m^{2/3}t^{1/6}$=1·381 mg.$^{2/3}$ sec.$^{-1/2}$		50% dioxane (by volume) $m^{2/3}t^{1/6}$=1·455 mg.$^{2/3}$ sec.$^{-1/2}$		50% acetone (by volume) $m^{2/3}t^{1/6}$=1·398 mg.$^{2/3}$ sec.$^{-1/2}$	
Conc. of *o*-iodobenzoic acid (millimolar)	Diffusion current constant (I)	Conc. of *o*-iodobenzoic acid (millimolar)	Diffusion current constant (I)	Conc. of *o*-iodobenzoic acid (millimolar)	Diffusion current constant (I)
0·300	2·30	0·660	2·50	0·751	3·27
0·600	2·31	1·336	2·49	1·502	3·25
1·412	2·29	2·005	2·49	3·122	3·25
2·582	2·28	2·673	2·48	5·400	3·24
6·040	2·28	5·346	2·48	6·800	3·24
10·34	2·28	8·018	2·47	10·00	3·23

The constancy of the diffusion current constant in the different solvents indicate that the polarographic method can be employed for the estimation of *o*-iodobenzoic acid.

4. $I\sqrt{\eta}$ *relationship.*—In Table IV are given the values of $I\sqrt{\eta}$ for *o*-iodobenzoic acid in all the three solvents at pH 11. For purposes of comparison the values calculated for iodobenzene[1] and 2-iodonaphthalene[2] have been placed together in the same table. Examination of the results presented in Table IV indicates that in the case of iodobenzene $I\sqrt{\eta}$ increases while in the case of iodonaphthalene there is only a slight increase. In the case of *o*-iodobenzoic acid, however, the changes are not very pronounced and can be taken to be fairly constant.

5. *Calculation of the number of electrons involved in the reduction process by Ilkovic Equation.*—The number of electrons involved in the reduction

TABLE IV

Values of $I\sqrt{\eta}$ for o-iodobenzoic acid, iodobenzene and 2-iodonaphthalene in different solvents

Solvent	% by volume of solvent	$I\sqrt{\eta}$		
		o-iodobenzoic acid	iodobenzene	2-iodonaphthalene
Ethanol ..	0	3·69	..	..
	10	3·69	0·78	2·79
	25	3·85	1·68	3·23
	50	3·25	3·63	3·79
	75	3·37	4·37	4·04
	98	3·26	6·33	4·12
Dioxane ..	10	3·98	1·63	2·59
	25	3·74	2·78	3·00
	40	..	3·35	3·46
	50	3·50	3·74	3·72
	60	..	3·94	3·80
	75	3·29	..	..
Acetone ..	10	3·83	1·40	3·39
	20	..	2·49	3·62
	25	3·59	3·07	3·76
	50	3·72	3·86	3·81
	60	..	4·15	3·78
	75	3·80	..	..

process has been calculated from the Ilkovic Equation using the values of the diffusion coefficients obtained by the diaphragm cell, equivalent conductivity and viscosity methods and the results are presented in Table V. It can be seen from the table that the value of '*n*' is consistently near 2 only when the diffusion coefficients from the diaphragm cell method are used for calculating the value of '*n*'.

DISCUSSION

1. *Effect of pH on the diffusion current constant and half-wave potential at various concentrations of the organic solvent.*—Gergely and Iredale[10] have stated that below pH 3, *o*-iodobenzoic acid exists as the undissociated acid and above pH 7 only as the ions. In the intermediate pH range both the

TABLE V

Number of electrons involved in the reduction of o-*iodobenzoic acid in aqueous mixtures of ethanol, dioxane and acetone calculated employing the diffusion coefficients from diaphragm cell, conductivity and viscosity methods*

Organic solvent	% by volume of organic solvent	'n' calculated from the diffusion coefficient by		
		diaphragm cell method	conductivity method	viscosity method
Ethanol ..	0	1·9	2·1	2·6
	10	1·9	1·9	2·6
	25	2·0	1·6	2·7
	50	2·0	1·2	2·3
	75	2·0	1·2	2·4
	98	2·0	1·2	2·4
Dioxane ..	10	1·9	2·1	2·8
	25	2·0	1·7	2·6
	50	1·9	1·3	2·5
	75	1·9	1·1	2·3
Acetone ..	10	1·9	2·0	2·7
	25	1·9	1·8	2·5
	50	2·0	1·8	2·6
	75	2·0	1·7	2·7

undissociated acid and the ions are present. The half-wave potential of the undissociated acid is $-1{\cdot}14$ V. *vs.* S.C.E. while that of the ion is $-1{\cdot}60$ V. *vs.* S.C.E. In buffer solutions, however, they have noticed only one wave. In base solutions containing potassium chloride and 5% ethanol, they have observed two waves, corresponding to the reduction of the undissociated acid and the ion. When the base solution contains 66% ethanol and 0·1 M tetraethyl ammonium bromide, the height of the first wave increases at the expense of the second, obviously due to the suppression of the dissociation.

In the present work our studies have been confined only to buffer solutions and the effect of organic solvents on the diffusion current constant and the half-wave potential have been investigated. In this connection it may be pointed out that the pH of the buffer solution as indicated by the hydrogen electrode shifts to higher pH values with the addition of organic

reagent. For example, the pH of acetate buffer of pH 5·1 in aqueous media was found to be 5·9 in 90% ethanol. When the concentration of ethanol is less than 75% the change in pH between aqueous and alcoholic solutions is very much less. The behaviour is similar even in presence of dioxane and acetone.

The change in the diffusion current constant with an increase in the concentration of ethanol may be due to a variation either of the diffusion coefficient or the proportion of undissociated acid or both. In alkaline solutions, however, the variation of the diffusion current constant is due only to the variation in the diffusion coefficient since all the iodobenzoic acid is present in the form of ions ($I \alpha D^{\frac{1}{2}}$). At pH 3·3, the ratio of the diffusion current constant at 98% ethanol and 25% ethanol is 0·91, while the corresponding ratio of the sq. root of the diffusion coefficients (Table II) is 0·74. A difference between these two values can be due to (i) increase in pH by the addition of alcohol and (ii) decrease in the dissociation constant of iodobenzoic acid. An increase in pH would favour the formation of iodobenzoate ion while the fall in the dissociation constant of the acid would have the opposite effect. Since the experimental results indicate a suppression of the dissociation, it can be concluded that this effect predominates over the first.

In solutions containing dioxane and acetone (pH 3·3) the half-wave potentials at 75% concentration of the organic solvent are — 1·59 and — 1·62 V. *vs.* S.C.E. respectively. It is surprising that the shifts are so marked in these two solvents. Calculations, similar to those given in the case of alcohol, made between 75% and 25% of dioxane and acetone, indicate that there is slight suppression of dissociation of the iodobenzoic acid in these solvents.

As indicated already, above pH 7 it is only the ion that is getting reduced. It is significant that there is no variation either in the diffusion current constant or in the half-wave potential when pH is altered.

2. *Relationship between the diffusion coefficient by the diaphragm cell method and the diffusion current constant at various concentrations of organic solvent.*—As already indicated the relationship between the diffusion current constant and the diffusion coefficient has been tested only at pH 11. It is significant that both the diffusion current constant and the diffusion coefficient (as determined by the diaphragm cell method) decrease with an increase in the concentration of the organic solvent. On graphical analysis, it is found that $I \alpha D^{\frac{1}{2}}$ is in agreement with the Ilkovic Equation. It is noteworthy that irrespective of the increase (as in the case of iodobenzene[1]) or the decrease

of the diffusion current constant with solvent concentration, the relationship $I \alpha D^{\frac{1}{2}}$ always holds good.

3. *Reversibility of the electrode process.*—The values of $E_{\frac{1}{4}}-E_{\frac{1}{4}}$ of all the polarographic waves obtained under different conditions are of the order of 0·1 V. indicating that the reduction process is irreversible in character.

4. *$I\sqrt{\eta}$ relationship.*—In the case of iodobenzene it has been found that the diffusion coefficient by the viscosity method decreases with an increase in the concentration of the organic solvent while the diffusion current constant increases. On the other hand, in the case of *o*-iodobenzoic acid both the diffusion current constant and the diffusion coefficient decrease with an increase in the concentration of the organic solvent. Based on Stokes-Einstein Diffusion Equation and the Ilkovic Equation[11] it has been shown that $I\sqrt{\bar{\eta}} =$ constant, where changes of diffusion coefficients are solely due to variations in the viscosity of the base solution. The values of $I\sqrt{\bar{\eta}}$ for *o*-iodobenzoic acid are given in Table IV and for purposes of comparison $I\sqrt{\eta}$ for iodobenzene and iodonaphthalene are also included in the table. It is clear that in the case of *o*-iodobenzoic acid the values of $I\sqrt{\bar{\eta}}$ are practically constant as compared to those of iodobenzene and iodonaphthalene. In the case of iodobenzene and iodonaphthalene where $I\sqrt{\bar{\eta}}$ is not a constant the values of '*n*' calculated on the basis of the diffusion coefficient from viscosity data lead to erroneous conclusions. Even in the case of iodobenzoic acid where $I\sqrt{\bar{\eta}}$ is fairly constant the value of '*n*' is not equal to two. This shows that not much reliance can be placed on the values of the diffusion coefficients from viscosity data. The inapplicability of the conductivity data for the determination of '*n*' is shown by the results presented in Table V where the value of '*n*' changes from 1·2 to 2·1 at different concentrations of the organic solvent. It is important to note that the values of '*n*' calculated by employing the diffusion coefficients obtained by the diaphragm cell method are very nearly two under all conditions.

The mechanism of the reduction process can therefore be written as follows:—

$$C_6H_4.I.COOH + 2e + H^+ \rightarrow C_6H_5.COOH + I^-$$

Similar conclusions have also been arrived at by Gergely and Iredale[10] for the reduction by large-scale electrolysis.

Summary

The polarographic behaviour of *o*-iodobenzoic acid has been studied in aqueous mixtures of ethanol, dioxane and acetone at different acidities. It has been found that the diffusion constant current decreases with an increase

in the concentration of the organic solvent at all pH values. Above pH 7, the diffusion current constants at different pH values are nearly equal indicating that it is only the ion that is getting reduced. At pH 3·3 evidence has been obtained for the formation of a larger amount of the undissociated acid with an increase in the concentration of the organic solvent. The diffusion coefficients have been determined using the diaphragm cell technique and the number of electrons involved in the reduction process, as calculated from the Ilkovic equation on the basis of these diffusion coefficients, is found to be two under all experimental conditions. It has been shown that though the value $I\sqrt{\eta}$ is fairly constant, the diffusion coefficients calculated from viscosity data lead to erroneous conclusions regarding the reduction mechanism. It has also been found that the diffusion coefficients derived from conductivity data are also not useful for elucidating the mechanism of the reduction process. The half-wave potential increases to more negative values with an increase in the concentration of the organic solvent and the values of $E_{\frac{1}{2}}-E_{\frac{1}{4}}$ indicate that the electrode process is irreversible in character.

ACKNOWLEDGEMENT

The authors wish to express their sincere thanks to Prof. K. R. Krishnaswami and Prof. M. R. A. Rao for their helpful discussions.

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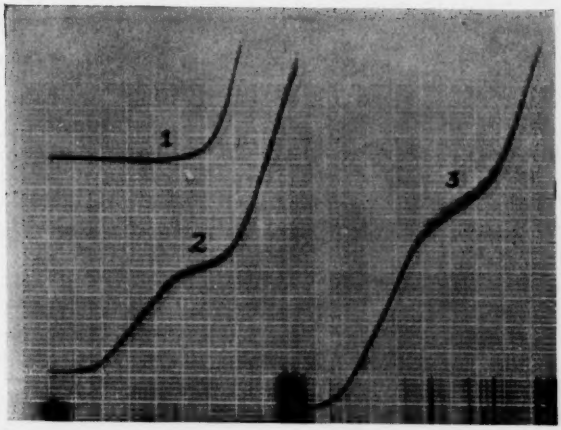

FIG. 1. Polarograms of *o*-iodobenzoic acid in 25% dioxane with 0·5 M lithium chloride and 0·002% gelatin at pH 3·3. Sensitivity: S/200. Curve 1 is blank; curves 2 and 3 are obtained with $3{\cdot}32 \times 10^{-3}$ M and $6{\cdot}64 \times 10^{-3}$ M *o*-iodobenzoic acid respectively. The voltage line just before each polarogram corresponds to $-0{\cdot}873$ V. *vs.* S.C.E.

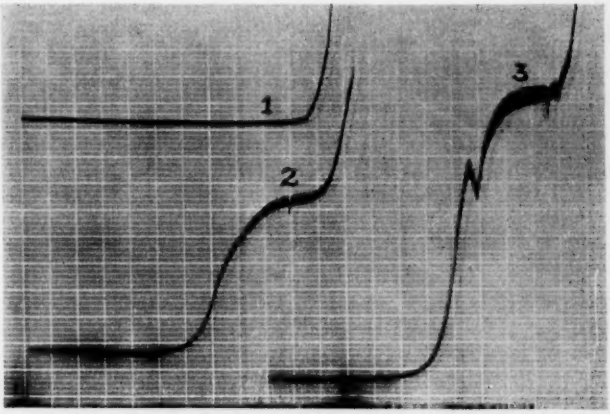

FIG. 2. Polarograms of *o*-iodobenzoic acid in 25% ethanol with 0·5 M lithium chloride at pH 9. Sensitivity: S/70. Curve 1 is blank; curves 2 and 3 are obtained with $1{\cdot}387 \times 10^{-3}$ M and $2{\cdot}774 \times 10^{-3}$ M *o*-iodobenzoic acid respectively. The voltage line preceding each polarogram corresponds to $-0{\cdot}873$ V. *vs.* S.C.E.

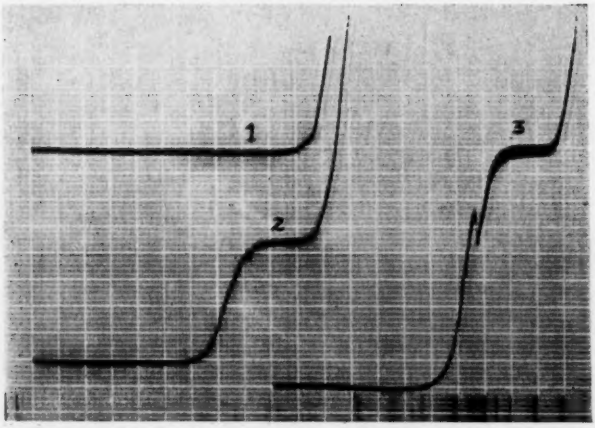

FIG. 3. Polarograms of *o*-iodobenzoic acid in 50% dioxane with 0·5 M lithium chloride at pH 11. Sensitivity: S/50. Curve 1 is blank; curves 2 and 3 are obtained with $0{\cdot}984 \times 10^{-3}$ M and $1{\cdot}967 \times 10^{-3}$ M *o*-iodobenzoic acid respectively. The voltage line preceding each polarogram corresponds to − 0·873 V. *vs.* S.C.E.

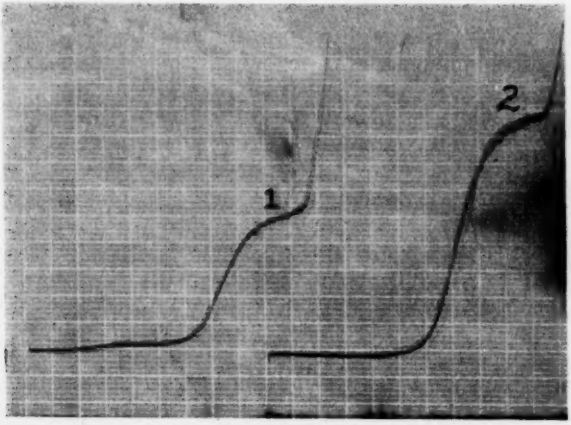

FIG. 4. Polarograms of *o*-iodobenzoic acid in 25% acetone with 0·5 M lithium chloride, 0·001% gelatin at pH 11. Sensitivity: S/70. Curves 1 and 2 are obtained with $1{\cdot}05 \times 10^{-3}$ M and $2{\cdot}10 \times 10^{-3}$ M *o*-iodobenzoic acid respectively. The voltage line preceding each polarogram corresponds to − 0·873 V. *vs.* S.C.E.

LEUCOANTHOCYANIDIN-(FLAV-3-ENE-3-OL) ACETATES

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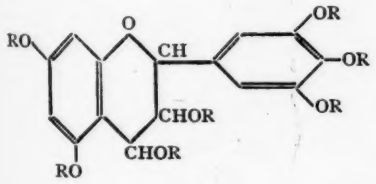
(*Department of Chemistry, Delhi University, Delhi*)

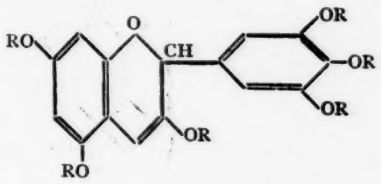
Received September 18, 1958

The conversion of leucoanthocyanidins of the flavan-3: 4-diol type into the corresponding anthocyanidins gives very poor yields[1] (ca. 10%). In the course of our studies on leucoanthocyanidins obtained from various natural sources and by synthetic means, we have obtained certain results which are significant in that they offer a method of obtaining better yields in the above-mentioned conversion. For example a sample of leucodelphinidin (flavan-diol, I A) from *Phyllanthus emblica* bark[2] gave a normal heptaacetate (II) when acetylated in the cold with acetic anhydride and pyridine. On the other hand, an isomeric leucodelphinidin (flavan-diol, IB) isolated from *Myrica nagi* bark[3] when acetylated in the same way yielded a different compound which was a hexaacetate agreeing with the requirements of a flav-3-ene-3-ol acetate (III). On boiling with alcoholic hydrochloric acid it gave a comparatively high yield of delphinidin (IV). The leucodelphinidin (I A) could also be converted into its flav-3-ene-3-ol acetate by two stage acetylation, *i.e.*, first in the cold followed by heating the reaction mixture. This was found to be the same as the one obtained from (I B), and also gave a good yield of delphinidin chloride (IV). The two leucodelphinidins mentioned above represent two different stereo-isomers, (I B) being capable of losing the elements of water even in the cold and (I A) doing so only on heating. These experiments also show that flav-3-ene-3-ol acetates are good intermediates for the conversion of flavan-3: 4-diols into anthocyanidins.

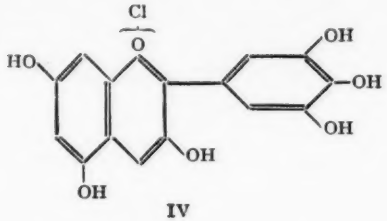


I, R=H

II, R=$COCH_3$

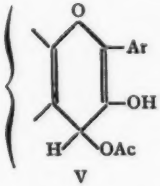


III, R=$COCH_3$

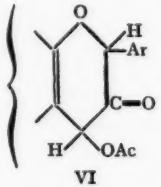


IV

In this connection should be mentioned certain observations which are of significance for the present subject. Robertson and Robinson[4] earlier carried out the reduction of rhamnetin by short boiling (7 to 8 minutes) with acetic anhydride, potassium acetate and zinc dust. The crude product was boiled with alcoholic hydrochloric acid giving a small yield of rhamnetinidin chloride besides polymerised products. Malkin and Nierenstein[5] repeated the process using only zinc and acetic anhydride and reported that they obtained only polymeric products from quercetin and rhamnetin. Recently King and White[6] described their results on the reductive acetylation of quercetin and other flavonols using acetic anhydride, sodium acetate and zinc dust and boiling for two hours. Though in each case the nature of the product was not clear and it did not have a sharp melting point, it underwent conversion into the corresponding anthocyanidin in good yields. The important point that they noted was that the intermediate compound had the same number of acetoxyl groups as the acetate of the original flavonol and that the reduction had not resulted in the increase of a hydroxyl or acetoxyl group. For example the product from quercetin had only five acetoxyl groups. King and White[6] gave (V) and (VI) as the probable structures for the reductively acetylated intermediate. Their suggestion seems to be that the carbonyl group of the flavonol alone underwent reduction yielding a derivative of anthocyanidin pseudo-base, and that one hydroxyl group escaped acetylation. But the analytical results do not agree with the proposed formula.



V



VI

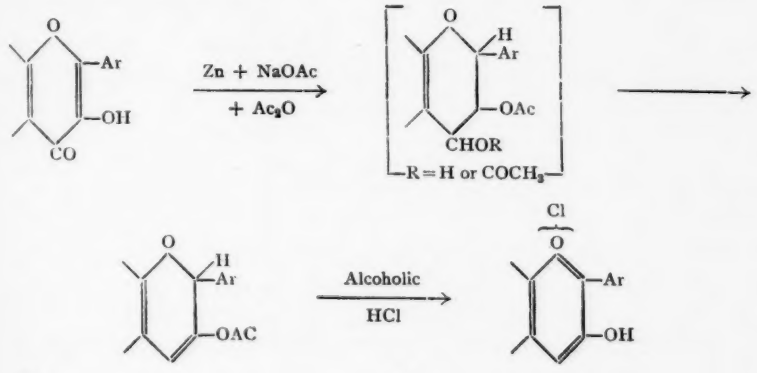
It appeared to us that the reductive acetylation procedure gave rise to flave-3-ne-3-ol acetates that have been mentioned in the earlier paras. Not

only is there close resemblance in physical properties, but the idea is fully supported by the analytical results reported by King and White.[6] The comparative data in the case of fisetin and quercetin (King and White[6]) and myricetin (present work) are given in Table I.

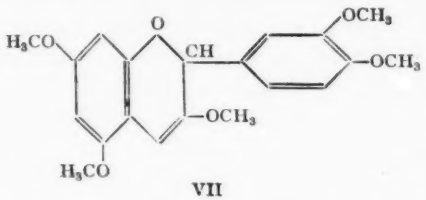
TABLE I

1	2	3	4	5	6
Original flavonol	King and White's formula for the reductive acetylation product	% Required for (2)	% Found	% Required for (6)	Present flav-3-ene-3-ol acetate formula
Fisetin	$C_{23}H_{20}O_{10}$	C, 60·5; H, 4·4	C, 62·6; H, 4·5	C, 62·6; H, 4·5	$C_{23}H_{20}O_9$
Quercetin	$C_{25}H_{22}O_{12}$	C, 58·2; H, 4·3	C, 59·8; H, 4·6	C, 60·2; H, 4·5	$C_{25}H_{22}O_{11}$
Myricetin	$C_{27}H_{24}O_{14}$	C, 56·6; H, 4·2	C, 58·0; H, 4·8	C, 58·3; H, 4·3	$C_{27}H_{24}O_{13}$

We now suggest the following explanation of the course of the reaction. The reduction could be visualised as affecting not only the carbonyl group but also the pyrone double bond. That the latter is actually more easily reduced is indicated by the earlier[7,8] finding that the reduction of chalkone with zinc dust and acetic acid yields dihydro-chalkone. The formation of the flavan-diol derivative is followed by the elimination of the elements of water giving rise to the proposed flav-3-ene-3-ol acetate. In the presence of alcoholic hydrochloric acid, deacetylation is accompanied by oxidation yielding the flavylium salt.



In support of the above may be mentioned the following points which do not agree with the formulation of King and White[6]: (i) Dihydroquercetin (taxifolin) in which the pyrone double bond is non-existent underwent reductive acetylation smoothly to yield the same acetate as was obtained from quercetin. The two products agreed in composition, melting point and infra-red spectrum. (ii) The reductive acetylation of myricetin gave a product which agreed with the leucodelphinidin-(flav-3-ene-3-ol) acetate obtained from the natural samples of leucodelphinidin isolated from *Phyllanthus emblica* and *Myrica nagi* in respect of infra-red spectrum and ready conversion into delphinidin chloride. As in other cases of reductive acetylation, the product had a lower and indefinite melting point and this may be due to the simultaneous formation of more than one isomer. (iii) Quercetin pentamethyl ether which does not contain any free hydroxyl group in 3-position underwent smooth reduction to give 3:5:7:3′:4′-pentamethoxy flav-3-ene (VII). This flavene had no acetoxyl group (as shown by the infra-red spectrum), contained all the five methoxyl groups intact and could be converted into pentamethyl cyanidin chloride.



VII

Earlier several methods were adopted for the reduction of flavonols leading to the formation of anthocyanidins. It seems to be possible that in all these cases the conjugated $O=\overset{|}{C}-C=\overset{|}{C}-$ system was hydrogenated to yield flavan-diols which under the conditions employed gave varying yields of anthocyanidin and phlobaphene.

EXPERIMENTAL

Leucodelphinidin—(flav-3-ene-3-ol) acetate

(i) The leucodelphinidin (I B) (0·3 g.) was suspended in acetic anhydride (10 c.c.) and then treated with dry pyridine (3 c.c.) to obtain a clear solution. After allowing it to stand at room temperature for 48 hours, it was poured over crushed ice with stirring. The colourless solid thus obtained was

filtered, dried and then crystallised from a mixture of ethyl acetate and light petroleum (40–60°) yielding tiny prisms (0·25 g.), m.p. 170–75° d (Found: C, 58·3; H, 4·6; $C_{27}H_{24}O_{13}$ requires C, 58·3; H, 4·3%).

(ii) As reported in a previous publication,[2] the cold acetylation of leucodelphinidin (I A) from *Phyllanthus emblica* bark yielded a leucodelphinidin heptaacetate, m.p. 240–45°. The two stage acetylation of this isomer has now been carried out as follows: The leucodelphinidin (I A) (0·2 g.) was dissolved in acetic anhydride (10 c.c.) and pyridine (2 c.c.), the solution left at the room temperature for 48 hours and then heated under reflux for 2 hours. There was some resinification during the heating. The mixture was poured over crushed ice and the dark solid that separated was collected and dried in a vacuum desiccator. It was dissolved in a small amount of ethyl acetate and the dark resinous impurities precipitated by the addition of a few drops of light petroleum (40–60°). Finally the almost colourless acetate was precipitated by the addition of excess of light petroleum. Crystallisation from a mixture of ethyl acetate and light petroleum gave rhombohedral plates (0·1 g.), m.p. 170–74° d (Found: C, 58·0; H, 4·8; $C_{27}H_{24}O_{13}$ requires C, 58·3; H, 4·3%). It agreed with the acetate form (i) in every respect.

Conversion into delphinidin chloride

The crude flav-3-ene-3-ol-acetate obtained in experiment (ii) from leucodelphinidin (I A) (0·4 g.) was converted into delphinidin chloride by heating with alcoholic hydrochloric acid as given below under (iii). The product (0·12 g.) was identical with delphinidin chloride.

(iii) *Reductive acetylation of myricetin.*—Myricetin (0·2 g.) was mixed with zinc dust (0·3 g.), fused sodium acetate (0·1 g.) and acetic anhydride (6 c.c.) and refluxed for 1 hour. The solution developed a red colour; more zinc dust (0·3 g.) was added and the refluxing continued for another hour. The mixture was filtered and the residue washed with small quantities of glacial acetic acid. The filtrate was poured over crushed ice and the separated solid filtered off. It was dissolved in a small quantity of glacial acetic acid and reprecipitated by the addition of water. It was then dried and finally purified from ethyl acetate and light petroleum (40–60°) yielding a colourless crystalline product (0·22 g.), m.p. 97–108° (Found: C, 58·4; H, 4·4; $C_{27}H_{24}O_{13}$ requires C, 58·3; H, 4·3%).

Conversion into delphinidin chloride

The above acetate (100 mg.) was refluxed with 10% alcoholic hydrochloric acid (25 c.c.) for 2 hours. Within 5 minutes the solution became

deep red. It was cooled, diluted with twice its volume of water and left in the refrigerator. The small quantity of dark red phlobaphene which had separated was filtered off and the filtrate extracted with isoamyl alcohol, which completely extracted the anthocyanidin chloride. The alcohol layer was washed with 1% aqueous hydrochloric acid. Finally more of 1% hydrochloric acid was added and the mixture shaken with a large excess of light petroleum (6 volumes). The aqueous acid solution was thoroughly washed with light petroleum and benzene to remove traces of isoamyl alcohol and then concentrated in a vacuum desiccator over potassium hydroxide. The crystalline anthocyanidin chloride (40 mg.) obtained agreed with delphinidin chloride in every respect. A drop of the 1% hydrochloric acid extract was subjected to circular paper chromatography using phenol-water (lower layer) as the irrigating solvent at 30°; a ring was observed with an Rf 0·55. A 0·1% methanolic hydrochloric acid extract of the anthocyanidin chloride showed a maximum at 540 mμ in the visible region. Its colour reactions agreed with those of delphinidin chloride fully.

Leucocyanidin-(flav-3-ene-3-ol) acetate (reductive acetylation of dihydroquercetin)

The reductive acetylation of dihydro-quercetin (0·2 g.) was carried out and the product purified in the same way as that from myricetin. The colourless tiny prisms (0·22 g.) melted at 90–100° (Found: C, 60·4; H, 5·0; $C_{25}H_{22}O_{11}$ requires C, 60·2; H, 4·5%). It agreed in analytical values and infra-red spectrum with the leucocyanidin—(flav-3-ene-3-ol) acetate obtained by the reductive acetylation of quercetin.

Conversion into cyanidin chloride

The above acetate (100 mg.) was converted into cyanidin chloride (45 mg.) in the same way as described for delphinidin chloride above. A drop of the acid solution of the anthocyanidin chloride when subjected to horizontal paper chromatography (phenol-water lower layer), gave Rf 0·72 at 30°. The anthocyanidin chloride showed an absorption maximum at 523 mμ in the visible region.

3:5:7:3′: 4′-*Pentamethoxy flav-3-ene (reduction of quercetin pentamethyl ether)*

Quercetin pentamethyl ether (0·2 g.) was subjected to reductive acetylation as in the case of myricetin. The product came out from ethyl acetate-light petroleum as colourless tiny prisms, m.p. 80–90° (Found: C, 63·9; 64·2; H, 6·1; 6·0; OCH_3 41·9; $C_{20}H_{22}O_6$, $1H_2O$ requires C, 63·8; H, 6·4; OCH_3, 43·1%). The flavene pentamethyl ether (100 mg.) was treated

with alcoholic hydrochloric acid in the same way as with leucocyanidin (flav-3-ene-3-ol) acetate. The product (25 mg.) melted at 148–50°. Pratt and Robinson[9] reported m.p. 152° for pentamethyl cyanidin chloride.

Summary

Leucodelphinidin (flavan-diol, I B) under mild conditions of acetylation and another leucodelphinidin (flavan-diol, I A) under more drastic conditions yield the same flav-3-ene-3-ol acetate which produces delphinidin chloride in much better yields than the original diols. Products of reductive acetylation of flavonols agree with flav-3-ene-3-ol acetates in important respects. Reductive acetylation of dihydro-quercetin yields the same product as that of quercetin. Quercetin pentamethyl ether suffers similar reduction under the same conditions. It is therefore concluded that reductive acetylation reduces both the ethylenic and carbonyl groups and is followed by loss of the elements of water.

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